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6. AUTHORS Timothy Swager			5d. PROJECT NUMBER		
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14. ABSTRACT This contract supported the development of fluorescence-based sensory methods for the standoff detection of explosives. In a subset of these technologies electronic (conjugated) polymers serve to amplify analyte-induced signals. New polymers were developed with different electronic structures/electron affinities to produce specific responses to classes of molecules. Organization schemes were developed to create materials with enhanced absorptions and strong narrow emissions. Methods to stabilize polymers from photobleaching were developed					
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## Report Title

### ABSTRACT

This contract supported the development of fluorescence-based sensory methods for the standoff detection of explosives. In a subset of these technologies electronic (conjugated) polymers serve to amplify analyte-induced signals. New polymers were developed with different electronic structures/electron affinities to produce specific responses to classes of molecules. Organization schemes were developed to create materials with enhanced absorptions and strong narrow emissions. Methods to stabilize polymers from photobleaching were developed based upon small molecule additives. Specific transduction methods were developed for the detection of nitro-amide and nitro-ester groups, found in the high explosives RDX and PETN. In these schemes the photochemical transformation (sunlight) causes a reaction sequence between the sensory material and the explosives that generates a new, highly specific, sensory signal. These potentially standoff optical methods were shown to be robust with sensitivity limits that match present day (stationary) explosives equipment based upon ion mobility spectrometers. Novel polymers were developed for the fluorescent detection of peroxides. New standoff methods for the detection of the aromatic components of fuel oil and diesel fuel were developed that made use of the use of a strongly optical absorbing complex with a highly specific indicator. In these methods two laser beams are used, and one is attenuated by the complex to produce a signal that is a ratio of the intensities.

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### List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

#### (a) Papers published in peer-reviewed journals (N/A for none)

Andrew, T. L.; Swager, T. M. "Reduced Photobleaching of Conjugated Polymer Films Through Small Molecule Additives" *Macromolecules* 2008, 41, 8306-8308.

Moslin, R. M.; Andrew, T. L.; Swager, T. M. "Anionic Oxidative Polymerization: The Synthesis of Poly(phenylenedicyanovinylene) (PPCN2V)" *J. Am. Chem. Soc.* 2009, 131, 20-21.

Moslin, R. M., Espino, C. G.; Swager, T. M. "Synthesis of Conjugated Polymers Containing cis-Phenylenevinylenes by Titanium Mediated Reductions" *Macromolecules* 2009, 42, 452-454.

Chan, J. M. W.; Tischler, J. R.; Kooi, S. E.; Bulovic, V.; Swager, T. M. "Synthesis of J-Aggregating Dibenzo[a,j]anthracene-Based Macrocycles" *J. Am. Chem. Soc.* 2009, 131, 5659-5666.

Andrew, T. L. VanVeller, Swager, T. M. "The Synthesis of Azaperylene-9,10-dicarboximides" *Synlett* 2010, 3045-3048

Number of Papers published in peer-reviewed journals: 5.00

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#### (b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

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#### (c) Presentations

Timothy M. Swager "Optical and Electrical Detection of Chemical Warfare Agents" ACS National Meeting in Washington DC, August 19, 2010.

Timothy M. Swager "Electronic Polymer-Based Chemical Sensors for Improved Security" Plenary Lecture, ACS Poly Division, ACS National Meeting in Washington DC, August 19, 2010.

Timothy M. Swager "Chemistry and Applications of Carbon Nanotubes" Invited Lecture at the International Korean-German Graduate School in Mainz, Germany, August 24, 2010.

Timothy M. Swager "Design, Synthesis and Sensory Applications of Electronic Polymers" and "Electronic Polymers and Molecular/Nano Wires for Chemical Sensing Workshop on Conducting Polymers" Hosted by the Academy of Sciences of the Czech Republic, Prague, The Czech Republic, September 14, 16, 2010.

Timothy M. Swager "Polymer Electronics for Chemical Sensors" 31st Princeton ACS Fall Organic Symposium, September 18, 2009.

Timothy M. Swager "Electronic Polymers for Chemical and Biological Sensing" Wright Patterson AFB, October 21, 2009

Timothy M. Swager "Optical and Electrical Detection of CW Agents and Implications of Nanoscience" Lecture to the Scientific Advisory Board of the Organization for the Prohibition of Chemical Weapons, The Hague, Holland, November 4, 2009

Timothy M. Swager "Triptycene: A Versatile Building Block for Sensory, Optical, Electronic, and Structural Polymers" and "Triptycene: A Versatile Building Block for Sensory, Optical, Electronic, and Structural Polymers" Northwestern University, Evanston Illinois, April 15, 2010

Timothy M. Swager "The Detection of Explosives and Chemical Weapons" and "Sensory Applications of Carbon Nanotubes" MacLean Lecture at MacMaster University, Hamilton Ontario, Canada, May 4 and 5, 2010

Timothy M. Swager "Polymer Electronics for Ultra-Sensitive Chemical Sensors" Chinese Chemical Society, July 14, 2008, Tainjin China

Timothy M. Swager "Polymer Electronics to Create Chemical Sensors" September 26, 2008, Department of Chemistry SUNY Stony Brook

Timothy M. Swager October 4, 2008, "Amplifying Polymers for Ultrasensitive Sensors" Department of Chemistry U. of Illinois Urbana Champaign

Timothy M. Swager "Polymer Electronics for the Creation of Chemical Sensors" October 10, 2008 Nakamoto Lecture, Department of Chemistry at Marquette University

Timothy M. Swager "Polymer Electronics for the Creation of Chemical Sensors" November 5, 2008, Department of Chemistry Central Michigan University

Timothy M. Swager "Amplifying Polymers for Ultrasensitive Sensors" Materials Research Society Meeting Dec. 3, 2008 Boston MA

Timothy M. Swager "Design of Responsive Conducting Polymers" Materials Research Society Meeting Dec. 4, 2008 Boston MA

Timothy M. Swager "Nanostructured Organic Electronic Materials for Chemical Sensing" December 16, 2008, US Japan Polymer Workshop Awaji Island Japan

Timothy M. Swager "Polymer Electronics for Chemical Sensors" January 16, 2009, U. of Texas Dallas

Timothy M. Swager "Polymer Electronics in the Design of Chemical Sensors" and "Iptycenes: Structures for the Design of New Materials" January 20 and 21, 2009, Barré Lectures University of Montreal

Timothy M. Swager "Polymer Electronics in the Design of Chemical Sensors" January 28, 2009, Department of Chemistry U. of Cal. Irvine

Timothy M. Swager "Amplifying Polymers for Ultrasensitive Sensors" February 6, 2009 Powell Lecture Department of Chemistry University of Richmond

Timothy M. Swager "Amplifying Polymers for Ultrasensitive Sensors" February 9, 2009, Department of Chemsitry Brandeis University

Timothy M. Swager "Iptycenes in the Design of New Materials " March 22, 2009, 237th National Meeting of the American Chemical Society, Salt Lake City, Utah

Timothy M. Swager "Chemiresistive Polymers and Materials for Chemical Sensors" March 23, 2009, 237th National Meeting of the American Chemical Society, Salt Lake City, Utah

Timothy M. Swager "Amplifying Polymers for Ultrasensitive Sensors" March 24, 2009 237th National Meeting of the American Chemical Society, Salt Lake City, Utah

Timothy M. Swager "Unique molecular architectures enabling new polymer applications" March 24, 237th National Meeting of the American Chemical Society, Salt Lake City, Utah

Timothy M. Swager "Chemical Sensing with Amplifying Fluorescent Polymers" May 4, 2009, Department of Chemistry University of Geneva, Switzerland

Timothy M. Swager "Polymer Electronics in the Design of Chemical Sensors" and "Iptycenes: Structures for the Design of New Materials" May 5 and 6, 2009 Department of Chemistry University of Neuchatel, Switzerland

Timothy M. Swager "Chemiresistors Based on Molecular Wire Principles" May 7, Department of Chemistry University of Berne, Switzerland

Timothy M. Swager "Synthetic Approaches to Electronic Polymers Electron Affinities" May 8, Department of Chemistry University of Lausanne, Switzerland

Timothy M. Swager "Luminescent Polymers and Materials for Sensing and Imaging" May 11, 2009 Department of Chemistry University of Basel, Switzerland

T. M. Swager “Fun with triptycenes: molecular shape in materials design” Montana State University, Bozeman 5/10/08 (Invited)

**Number of Presentations:** 30.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):** 0

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):** 0

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**(d) Manuscripts**

Andrew, T. L.; Swager, T. M. “Thermally-Polymerized Rylene Nanoparticles” Submitted

Andrew, T. L.; Swager, T. M. “Selective Detection of Explosives Via Photolytic Cleavage of Nitroesters and Nitramines” Submitted.

**Number of Manuscripts:** 2.00

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**Patents Submitted**

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## Patents Awarded

### Awards

Elected to the National Academy of Sciences 2008

Honorary Doctorate Degree Montana State University 2008

Fellow of the Division of Polymer Chemistry (ACS) 2009

John Scott Award 2008,

### Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Jeewoo Lim	0.20
Eric Dane	0.95
Shuang Liu	0.50
Trisha Andrew	0.15
Jason Cox	0.35
Olesya Haze	0.10
Brett VanVeller	0.20
Joel Batson	0.15
<b>FTE Equivalent:</b>	<b>2.60</b>
<b>Total Number:</b>	<b>8</b>

### Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Andreas Lohr	0.05
Ryan Moslin	0.50
<b>FTE Equivalent:</b>	<b>0.55</b>
<b>Total Number:</b>	<b>2</b>

### Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Timothy M. Swager	0.15	Yes
<b>FTE Equivalent:</b>	<b>0.15</b>	
<b>Total Number:</b>	<b>1</b>	

### Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Dale Robinson	0.05
<b>FTE Equivalent:</b>	<b>0.05</b>
<b>Total Number:</b>	<b>1</b>

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ..... 0.00

### Names of Personnel receiving masters degrees

NAME

Total Number:

### Names of personnel receiving PhDs

NAME

Total Number:

### Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	
Caitlin McDowell	0.50	No
Steven Kooi	0.40	No
Rebecca Bjork	0.25	No
<b>FTE Equivalent:</b>	<b>1.15</b>	
<b>Total Number:</b>	<b>3</b>	

### Sub Contractors (DD882)

1 a. ICx Technologies Inc.

1 b. 215 First Street

Suite 104

Cambridge

MA

02142

Sub Contractor Numbers (c): 5710002341

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): Transitioned MIT material and methods technologies for stand-off explosive detection and defined s

Sub Contract Award Date (f-1): 10/1/2007 12:00:00AM

Sub Contract Est Completion Date(f-2): 9/30/2010 12:00:00AM

### Inventions (DD882)

### **Scientific Progress**

To inbed graphics, I have used the option of an attachment. Please see the file labeled Scientific Progress.

### **Technology Transfer**

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## Statement of the Problem

Luminescent sensory materials have enabled detection of explosives vapors in the battlefield. Point detectors developed around these luminescent materials called Fido<sup>TM</sup> are now established as an indispensable asset to soldiers in Iraq. The development of additional materials that are designed to be sensitive to a broad range of explosives enables a robust solution to standoff detection of explosives. The detection principles will be based on pre-seeding areas of interest with luminescent sensory particles followed by laser excitation of the particles and remote multi-channel spectroscopic monitoring. Particles can be designed to give strong emissive signals and simultaneously detect multiple classes of explosives (i.e. nitroaromatics, RDX, PETN, peroxides, etc.) in multiplexed schemes. A particular advantage of this method is that the particles will respond to vapors emanating from the explosives. This response will create a large signature (multiple square meters) and optical detection do not require a line of sight directly to the explosive device. The expanded target reduces the density of the pattern to be rastered by the excitation lasers and thereby allow for more robust and rapid detection than a system that must directly illuminate the explosive device. Standoff detection methods have been initially demonstrated with particles containing novel sensory materials developed at MIT for TNT, PETN, RDX and fuel oil detection. Additional explosives detection materials will be developed to sense other explosives and to optimize standoff detection by tailoring the spectral characteristics of the sensory particles (wavelength, lifetime, etc.). This team will demonstrate reliable indication of the location of explosives in complex environments at distances greater than 100 meters. To enhance standoff detection different optical methods were developed, downselected, and optimized that make use of luminescence depolarization, lifetime modulation, ratiometric multiwavelength detection and excitation at eye-safe wavelengths.

## Summary of the Most Important Results

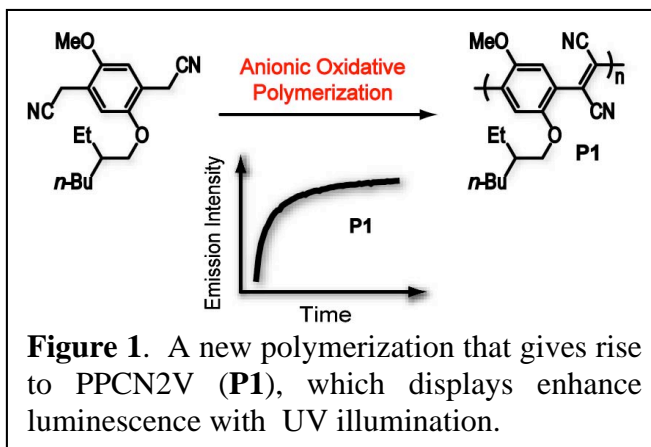
### *Stabilization of Polymer Sensors for Outdoor Applications*

Methods were developed to reduce polymer bleaching under direct sunlight. A number of additives were produced that worked as either to react with reactive oxygen species or to deactivate the triplet states of the polymers that give rise to the degradation pathways. Small molecule additives that act as either radical traps or triplet quenchers were found to decrease the extent of photobleaching in thin films of a pentyptycene-containing poly(p-phenylene ethynylene) and poly(9,9-dioctylfluorene). Hydrogen atom donors, such as cycloheptatriene and *N,N*-dioctyl-1,4-dihydro-*o*-toluamide, preserved approximately 80% of the initial emission intensities of thin films after 30 and 60 minutes of continuous irradiation, respectively. Such radical traps are proposed to quench reactive radicals formed in thin films by photoionization of the polymers. Alkylated cyclooctatetraenes (COTs) functioned as efficient triplet quenchers and retained up to 95% of the initial emission intensities of thin films after 30 and 60 minutes of continuous irradiation, respectively. COTs are believed to improve the photostabilities by rapidly deactivating the triplet excited state of these polymers and thus hindering the sensitized formation of reactive singlet oxygen.

### New High Stability Conjugated Polymer Sensory Materials

A new polymerization technique that allows for the first-ever synthesis of poly(phenylenedicyanovinylene)s (PPCN2Vs) was developed. PPCN2Vs, with their high electron affinities and structural versatility, seem ideally suited to address the need for new n-type sensory polymers (Figure 1). Remarkably the polymers presented herein become more photoluminescent, in the thin film, under continuous irradiation. This behavior makes them attractive for utilization in exterior applications.

We also developed a novel process for the conversion of polymers containing alkynes to produce responsive all *cis*-poly(phenylenevinylene)s (PPVs). This technique was then applied to the reduction of a poly(phenyleneethynylene) (PPE) to provide the corresponding all-*cis* PPV polymer.

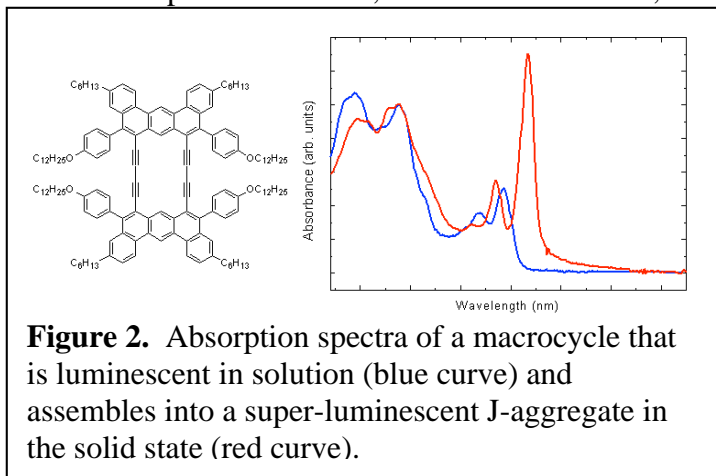


**Figure 1.** A new polymerization that gives rise to PPCN2V (**P1**), which displays enhance luminescence with UV illumination.

### Methods for Creating Ultra-Luminescent Materials

Several fluorescent macrocycles based on 1,3-butadiyne-bridged dibenz[*a,j*]anthracene sub-units have been synthesized via a multistep route. The synthetic strategy involved the initial construction of a functionalized dibenz[*a,j*]anthracene building block, subsequent installation of free alkyne groups on one side of the polycyclic aromatic framework, and a final cyclization based on a modified Glaser coupling under high-dilution conditions. Photophysical studies on three conjugated macrocycles revealed the formation of J-aggregates in thin films as well as in concentrated solid solutions (polyisobutylene matrix) with peak absorption and emission wavelength in the range of  $\lambda = 460$  nm to  $\lambda = 480$  nm (Figure 2). The characteristic red-shifting of the J-aggregate features as compared to the monomer spectra, enhancement in absorption intensities, narrowed linewidths, and minimal Stokes shift values,

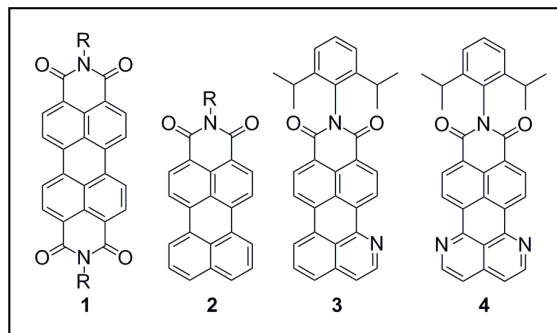
were all observed. We demonstrate that improvements in spectral features can be brought about by annealing the films under a solvent-saturated atmosphere, where for the best films the luminescence quantum efficiency as high as 92% was measured. This class of macrocycles represents a new category of J-aggregates that due to their high peak oscillator



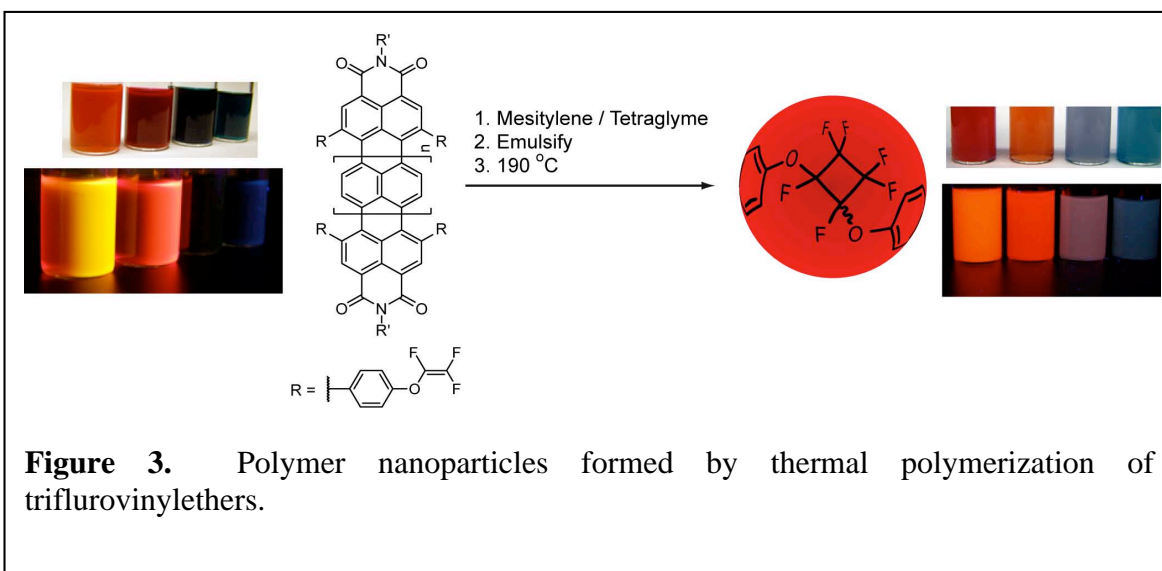
**Figure 2.** Absorption spectra of a macrocycle that is luminescent in solution (blue curve) and assembles into a super-luminescent J-aggregate in the solid state (red curve).

strength and high luminescence efficiency have the potential to be utilized in a variety of optoelectronic devices.

New azaperylene 9,10-dicarboximides **3** and **4** were developed as ultrastable far-red emitters. 1-Aza- and 1,6-diazaperylene 9,10-dicarboximides containing a 2,6-diisopropylphenyl substituent at the *N*-imide position were synthesized in two steps starting from naphthalene and isoquinoline derivatives. The eventual goal of these materials is to functionalize them to create long lifetime emitters for multiplexed (time gated) standoff sensing.



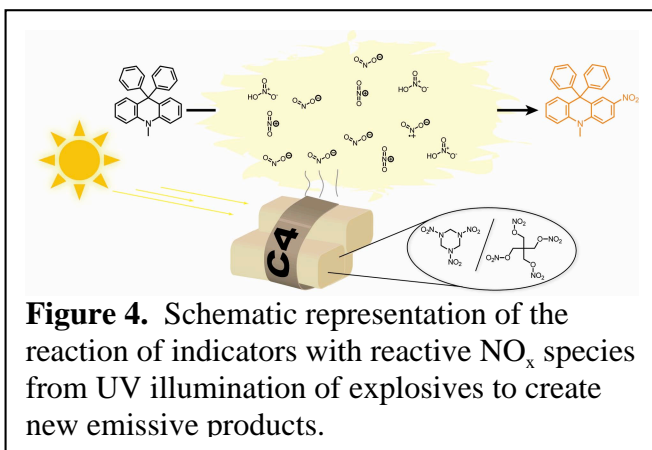
Rylene dyes functionalized with varying numbers of phenyl trifluorovinylether (TFVE) moieties were subjected to a thermal emulsion polymerization to yield shape-persistent, water-soluble chromophore nanoparticles. Perylene and terrylene diimide derivatives containing either two or four phenyl TFVE functional groups were synthesized and subjected to thermal emulsion polymerization in tetraglyme. Dynamic light scattering measurements indicated that particles with sizes ranging from 70 – 100 nm were obtained in tetraglyme, depending on monomer concentration. The photophysical properties of individual monomers were preserved in the nanoemulsions and emission colors could be tuned between yellow, orange, red, and deep red. The nanoparticles were found to retain their shape upon dissolution into water and the resulting water suspensions displayed moderate to high fluorescence quantum yield.



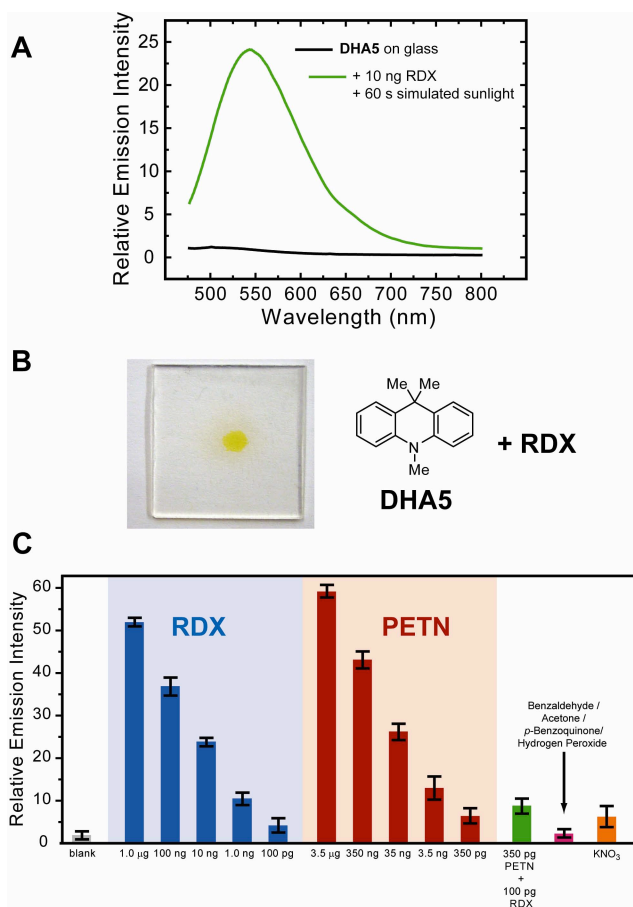
## Unique Transduction Chemistry for Nitroesters and Nitroamides

The nitramine-containing explosive RDX and the nitroester-containing explosive PETN are shown to be susceptible to photofragmentation upon exposure to sunlight. Model compounds containing nitroester and nitramine moieties are also shown to fragment upon exposure to UV irradiation. The products of this photofragmentation are reactive, electrophilic  $\text{NO}_x$  species, such as nitrous and nitric acid, nitric oxide,

and nitrogen dioxide. *N,N*-Dimethylaniline is capable of being nitrated by the reactive, electrophilic  $\text{NO}_x$  photofragmentation products of RDX and PETN. A series of 9,9-disubstituted 9,10-dihydroacridines (DHAs) are synthesized from either *N*-phenylanthranilic acid methyl ester or a diphenylamine derivative and are similarly shown to be rapidly nitrated by the photofragmentation products of RDX and PETN. A new (turn-on) emission signal at 550 nm is observed upon nitration of DHAs due to the generation of fluorescent donor-acceptor chromophores. Using fluorescence spectroscopy, the presence of ca. 1.2 ng of RDX and 320 pg of PETN can be detected by DHA indicators in the solid state upon exposure to sunlight. The nitration of aromatic amines by the photofragmentation products of RDX and PETN



**Figure 4.** Schematic representation of the reaction of indicators with reactive  $\text{NO}_x$  species from UV illumination of explosives to create new emissive products.



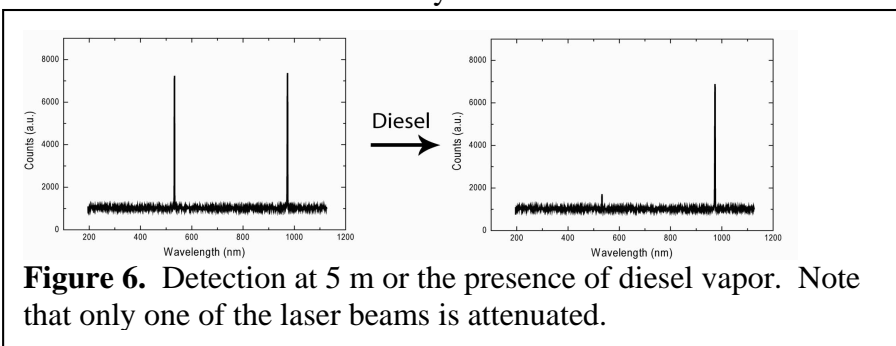
**Figure 5.** (A) Emission profile ( $\lambda_{\text{ex}}$  420 nm) of a glass slide coated with **DHA5** (black line) and the same slide after spotting with ca. 10 ng of RDX and irradiating with a solar simulator for 60 seconds (green line). (B) Picture of a glass slide coated with **DHA5**, spotted with ca. 10 ng RDX and exposed to simulated sunlight for 120 s. (C) Limits of solid-state detection of RDX and PETN as measured by monitoring the change in emission intensity at 540 nm upon exposure to simulated sunlight.



is presented as a unique, highly selective detection mechanism for nitroester- and nitramine-containing explosives and DHAs are presented as inexpensive and impermanent fluorogenic indicators for the selective, standoff/remote identification of RDX and PETN.

### ***Demonstration of Standoff Sensing and Imaging***

New methods for the detection of ANFO were investigated based upon the ability of 2,3-dichloro-5,5-dicyano-1,4-benzoquinone to form strong charge transfer complexes with alkylated aromatic compounds that are found in higher boiling fuels and oils. By using a two laser system and reflectors we were able to readily detect diesel fuel at a distance of 5 meters with simple lasers and a detector (Figure 6). It is expected that systems using retro-reflective devices could be readily fielded for this purpose.



Additional demonstrations were made for the disturbance of soil/sand and using simple filters and digital cameras, it was found that far red dyes and nanoparticles such as those described in this program could be readily imaged in daylight. Formulations that had a tacky (sticky) nature were developed to adhere to surfaces and shoes.

## **Appendixes**

The following publications have been attached.

### **Publication 1**

Andrew, T. L.; Swager, T. M. "Reduced Photobleaching of Conjugated Polymer Films Through Small Molecule Additives" *Macromolecules* **2008**, *41*, 8306-8308.

### **Publication 2**

Moslin, R. M.; Andrew, T. L.; Swager, T. M. "Anionic Oxidative Polymerization: The Synthesis of Poly(phenylenedicyanovinylene) (PPCN2V)" *J. Am. Chem. Soc.* **2009**, *131*, 20-21.

### **Publication 3**

Moslin, R. M., Espino, C. G.; Swager, T. M. "Synthesis of Conjugated Polymers Containing cis-Phenylenevinylens by Titanium Mediated Reductions" *Macromolecules* **2009**, *42*, 452-454.

Publication 4

Chan, J. M. W.; Tischler, J. R.; Kooi, S. E.; Bulovic, V.; Swager, T. M. "Synthesis of J-Aggregating Dibenz[a,j]anthracene-Based Macrocycles" *J. Am. Chem. Soc.* **2009**, *131*, 5659-5666.

Publication 5

Andrew, T. L. VanVeller, Swager, T. M. "The Synthesis of Azaperylene-9,10-dicarboximides" *Synlett* **2010**, 3045-3048

Publication 6

Andrew, T. L.; Swager, T. M. "Thermally-Polymerized Rylene Nanoparticles"  
Submitted

Publication 7

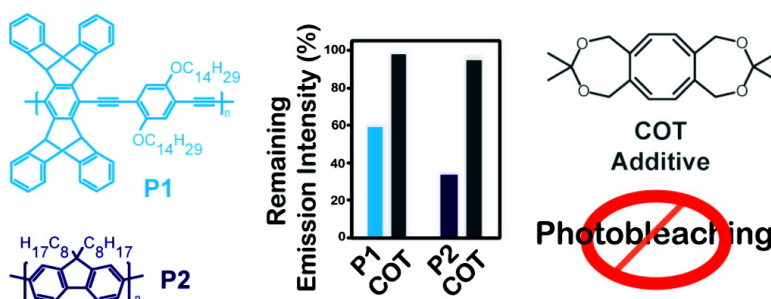
Andrew, T. L.; Swager, T. M. "Selective Detection of Explosives Via Photolytic Cleavage of Nitroesters and Nitramines" Submitted.

## Reduced Photobleaching of Conjugated Polymer Films through Small Molecule Additives

Trisha L. Andrew, and Timothy M. Swager

*Macromolecules*, **2008**, 41 (22), 8306-8308 • Publication Date (Web): 31 October 2008

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## Reduced Photobleaching of Conjugated Polymer Films through Small Molecule Additives

Trisha L. Andrew and Timothy M. Swager\*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

Received September 12, 2008

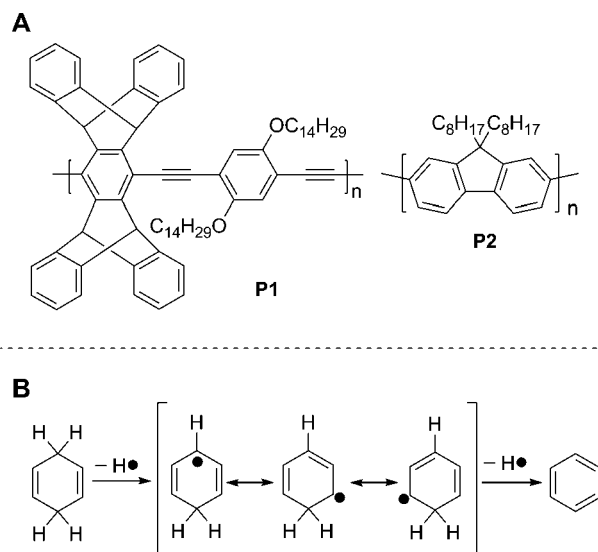
Revised Manuscript Received October 24, 2008

**Introduction.** The photobleaching, or reduction in fluorescence quantum yield, of fluorescent dyes upon continuous excitation is a commonly encountered problem.<sup>1</sup> The mechanism of photobleaching in fluorescent dyes has been shown to be complex, sensitive to environmental and excitation conditions, and specific to each dye.<sup>2</sup> Nevertheless, two primary pathways are invoked to explain the photodegradation of fluorophores.<sup>3</sup> In the first pathway, fluorophores are degraded by reaction with singlet oxygen, which is produced by sensitization of ground-state triplet oxygen by a small population of triplet-state fluorophores.<sup>4</sup> The second pathway involves reactive radical intermediates formed by the photoionization of fluorophores upon excitation to the first or higher excited electronic states in a polar environment.<sup>5</sup>

Photobleaching is observed in most fluorescent conjugated polymers (CPs), such as poly(phenylene)s (PPs),<sup>6</sup> poly(*p*-phenylenevinylene)s (PPVs),<sup>7</sup> and poly(*p*-phenylene ethynylene)s (PPEs),<sup>8</sup> in both solution and the solid state. In such polymeric systems, photooxidation of a few repeat units can create nonemissive traps capable of quenching any excitons formed in the polymer and, thus, decreasing its fluorescence quantum yield over time. This effect is most important in thin films wherein energy migration to nonemissive traps is most efficient.

Approaches to retard the photobleaching of fluorophores usually entail the introduction of small molecule additives (via either an admixture or a covalent linkage) specifically designed to counter one or both of the degradation pathways mentioned earlier. For example, antioxidants, such as ascorbic acid,<sup>3d,9</sup> *n*-propyl gallate,<sup>10</sup>  $\beta$ -mercaptoethanol,<sup>3d,11</sup> and cysteine hydrochloride,<sup>12</sup> are employed to trap reactive radicals in fluorophore solutions. Triplet quenchers, such as cyclooctatetraene (COT),<sup>3a,13</sup> mercaptoethylamine,<sup>3a</sup> and *trans*-stilbene (TS),<sup>3b,14</sup> are used to rapidly deactivate the triplet excited-state of fluorophores, which can otherwise sensitize the formation of singlet oxygen by energy (or electron) transfer to triplet oxygen. Tertiary amines,<sup>15</sup> especially 1,4-diazabicyclo[2.2.2]octane (DABCO),<sup>16</sup> are employed as singlet oxygen quenchers in solution. In this case, singlet oxygen formation is not inhibited, but the added DABCO is proposed to regenerate unreactive triplet oxygen from singlet oxygen via reversible electron transfer.

Surprisingly, the utility of such additives in curbing the photobleaching of CPs has not been thoroughly investigated. Since CPs find application in a variety of devices, for example, organic light-emitting diodes,<sup>17</sup> solar cells,<sup>18</sup> and optically pumped lasers,<sup>19</sup> and as fluorescent sensors for a wide array of analytes,<sup>20</sup> retarding photooxidation processes in these polymers is a topic of significant interest. Herein we investigate the effect



**Figure 1.** (A) Structures of the fluorescent polymers used in this work. (B) General approach for the design of antioxidants.

of added antioxidants and triplet quenchers on the photostabilities of thin films of a pentiptycene-containing PPE, **P1**, and poly(9,9-dioctylfluorene), **P2** (Figure 1A). The rational design and synthesis of antioxidants and triplet quenchers that are compatible with conjugated polymer films are also presented.

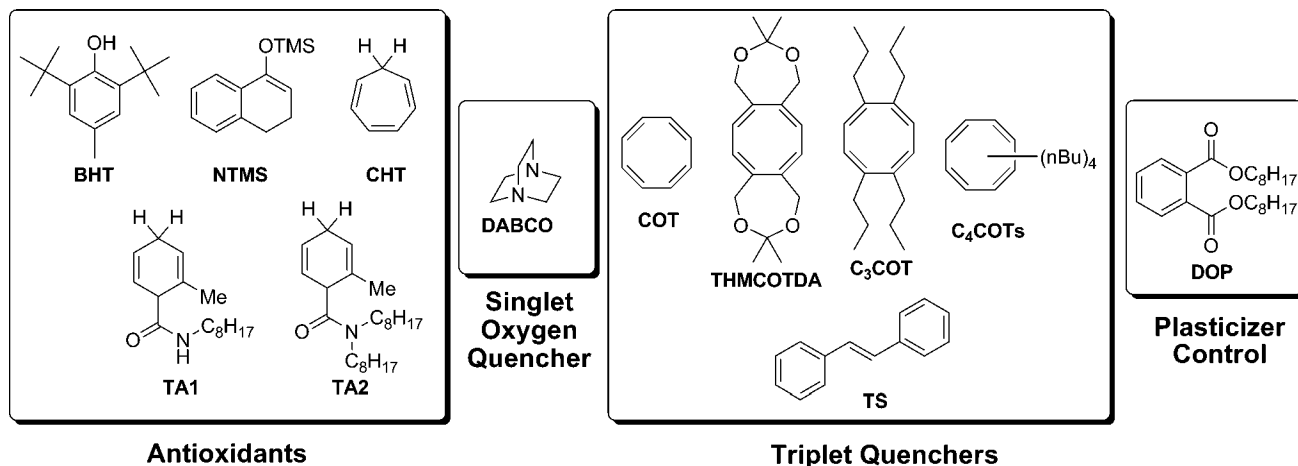
**Results and Discussion. Additive Design.** In choosing antioxidants to use with thin films of **P1** and **P2**, a major consideration is the solubility of the additives in the polymers, since phase separation of the additives will preclude any beneficial effects. Ascorbic acid and *n*-propyl gallate were not acceptable additives as they were insoluble in the PPE matrix; similarly, polar  $\beta$ -mercaptoethanol and ionic cysteine hydrochloride are not expected to be soluble in either **P1** or **P2**. Additionally, the oxidized form of the antioxidant, or the product of any reaction with reactive radicals, must not quench the fluorescence of **P1** or **P2**.

Adhering to these prescriptions, we proposed using a 1,4-dihydrobenzene moiety (Figure 1B) as the active component in antioxidants. 1,4-Dihydrobenzenes are predicted to quench any reactive radicals by liberating up to two hydrogen atoms ( $H^\bullet$ ), and the benzene thus produced will not quench the fluorescence of a conjugated polymer film. In addition, 2,6-di-*tert*-butyl-*p*-cresol (**BHT**) and cycloheptatriene (**CHT**) were also investigated as antioxidant stabilizers. It was anticipated that both the aryloxy radical and the tropylum cation generated by oxidation of **BHT** and **CHT**, respectively, will not quench the fluorescence of the polymers investigated.

To minimize the detrimental effects of singlet oxygen, a variety of COTs, including COT itself, and *trans*-stilbene (**TS**) were investigated as potential triplet quenchers. Since COT is volatile and does not exhibit thermal stability, some alkylated derivatives were synthesized to counter the evaporation of COT from thin films of **P1** and **P2**. Furthermore, the use of **DABCO** as a singlet oxygen quencher was also investigated.

The effects of the aforementioned additives on the emission intensities of **P1** and **P2** were compared against those of dioctyl phthalate (**DOP**), a common plasticizer, to confirm that any observed photostability does not arise from simple plasticization.

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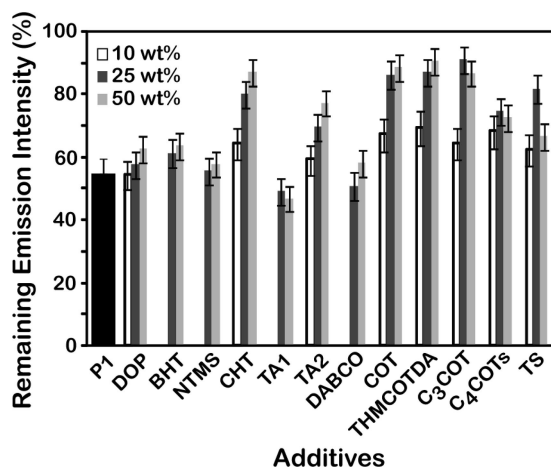


**Figure 2.** Structures of the small molecule additives investigated in this work.

**Synthesis.** Additives **BHT**, **NTMS**, **CHT**, **DABCO**, and **COT** and the dioctyl phthalate (**DOP**) plasticizer control (Figure 2) are commercially available. 1,4-Dihydro-*o*-toluamide additives **TA1** and **TA2** were synthesized in one-pot with 83% and 73% yields, respectively, from commercially available 1,4-dihydro-*o*-toluic acid via the acyl chloride (see Supporting Information). As previously reported, **THMCOTDA** was synthesized by a nickel(0)-catalyzed cyclo-tetramerization of propargyl alcohol and the isomer shown in Figure 2 isolated by formation of a diacetone.<sup>21</sup> **C<sub>3</sub>COT** was synthesized from **THMCOTDA** in three steps with 24% overall yield (see Supporting Information). Additionally, 1-hexyne was subjected to nickel(0)-catalyzed cyclization conditions to yield a mixture of four tetrabutyl-COT isomers (**C<sub>4</sub>COTs**, 82% by GC-MS analysis) and three tributylbenzene isomers (18%). The tetrabutyl-COT isomers could not be satisfactorily isolated from the cyclotrimers by column chromatography or separated by vacuum distillation without decomposition. Nevertheless, the mixture was investigated as an additive with the rationale that the tributylbenzene impurities will, at worst, serve as plasticizers for the polymer film.

**Polymer Thin Films.** Commercial **P2** was used without purification. Polymer **P1** was purified by multiple reprecipitations from methanol and washing with metal scavengers to exclude any impurities capable of giving rise to a false positive result. Thin films of **P1** and **P2** were spin-coated from chloroform solutions on 22 × 22 mm<sup>2</sup> glass substrates with either 25 or 50 wt % of each additive added to the spin-coating solutions. The uniformity of each thin film was confirmed by equivalent UV-vis absorption intensities from three different regions of the film. Photobleaching was accomplished by continuously irradiating ( $\lambda = 440$  nm for **P1**, 400 nm for **P2**) a 0.25 cm<sup>2</sup> area of the films with a 450 W Xe arc lamp under aerobic conditions with an average power density of 6.3 mW/cm<sup>2</sup>. The emission intensity at the emission maximum versus time was monitored for each polymer/additive combination over either 30 min (**P1**) or 60 min (**P2**) and the percent of photobleaching was calculated from the loss in fluorescence intensity at the maximum emission wavelength.

**Photobleaching.** Figure 3 shows a graph of the percent of the initial emission intensity that remains after the 30 min irradiation period for **P1**. Antioxidants **BHT**, **NTMS**, and **TA1** and the singlet oxygen quencher **DABCO** behaved similar to the plasticizer control **DOP** and therefore did not display a significant stabilization effect. However, antioxidants **CHT** and



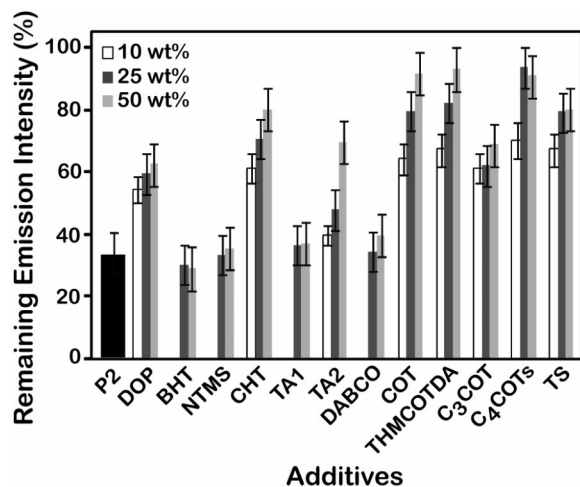
**Figure 3.** Percent remaining fluorescence intensity of thin films of **P1** mixed with either 10, 25, or 50 wt % stabilizers after irradiation for 30 min at 440 nm. The optical density of all the thin films was 0.1 ± 0.01.

**TA2** were effective at stabilizing **P1**, with up to 90 and 80% of the initial fluorescence retained after 30 min, respectively. The superior effectiveness of **TA2** over **TA1** is attributed to the improved miscibility of the *N,N*-dialkylamide moiety of **TA2** in the conjugated polymer matrix compared to the mono-*N*-alkylated amide of **TA1**. However, **TA2** was discovered to be significantly more susceptible to autoxidation than **TA1** and could not be stored for longer than approximately 1–2 months at −4 °C. Also, antioxidant **CHT** evaporated from spun-cast films with relative ease due to its volatility and therefore did not indefinitely impart photostability to thin films of **P1**.

Greater success was achieved with the use of triplet quenchers as stabilizing additives. Starting with **COT**, up to 90% of the initial emission intensity was conserved with 25 wt % of the additive. This result is echoed by both **C<sub>3</sub>COT** and **THMCOTDA**, the latter slightly surpassing **COT**. In comparison, the **C<sub>4</sub>COTs** underperformed with only 75% of the initial intensity remaining after 30 min; this is presumably due to the decreased COT content in the mixture and any counterproductive effects arising from the tributylbenzene impurities. Additionally, the presence of 25 wt % *trans*-stilbene displayed a moderately stabilizing effect on **P1**, although the effect was attenuated at a higher concentration.

Although the use of **COT** to stabilize thin films of **P1** suffered from the same evaporative loss encountered with **CHT**, tet-





**Figure 4.** Percent remaining fluorescence intensity of thin films of **P2** mixed with either 10, 25, or 50 wt % stabilizers after irradiation for 60 min at 400 nm. The optical density of all the thin films was  $0.1 \pm 0.01$ .

raalkylated **C3COT** and **THMCOTDA** proved effective solutions to this problem. Moreover, **THMCOTDA** exhibited remarkable thermal and chemical stability and did not noticeably phase separate from **P1** in thin films.

Concentration-dependent studies revealed that in all successful cases an additive concentration of at least 20 wt % was required to observe statistically significant stabilization. This observation is consistent with the practice of using high concentrations (ca.  $10^{-3}$  M) of similar additives to stabilize dilute solutions (ca.  $10^{-5}$  M) of fluorophores.<sup>9–16</sup> We hypothesize that since fluorescence stabilization by both triplet quenching and radical trapping is ultimately a diffusion-controlled process, a low additive concentration should not lead to significant suppression of photooxidation. Therefore, a small concentration of non-emissive traps will still be formed that are capable of quenching the excitons created in the thin film.

Figure 4 shows a graph of the percent of the initial emission intensity of **P2** that remains after 60 min of continuous irradiation. Similar to **P1**, a majority of the investigated antioxidants had a negligible effect on the photostability of **P2**, but **CHT** and **TA2** preserved 80% and 70% of the initial emission intensity, respectively. The stabilizing effects of **TA2** proved to be markedly dependent on concentration, with 50 wt % of the additive necessary to observe meaningful photostabilization.

Also in keeping with previous observations, the COT triplet quenchers—specifically **COT**, **THMCOTDA**, and **C4COTs**—proved most successful in stabilizing **P2**. Surprisingly, the **C4COTs** were reproducibly superior to **C3COT** in retarding photobleaching in **P2**; we are currently unsure as to the origin of this observation. Lastly, as with **P1**, the COT additives did not noticeably phase separate from thin films of **P2**, and at least 20 wt % of most additives was necessary to observe statistically significant stabilization.

**Conclusions.** Hydrogen atom donors, cycloheptatriene (**CHT**) and *N,N*-dioctyl-1,4-dihydro-*o*-toluamide (**TA2**), and a variety of cyclooctatetraene triplet quenchers effectively retarded the extent of photobleaching in thin films of a poly(*p*-phenylene ethynylene) and poly(fluorene). **CHT** and **TA2** preserved up to 80% of the initial emission intensities of both polymers after either 30 or 60 min of continuous irradiation. Tetraalkylated

**COTs**, **C3COT**, **C4COTs**, and **THMCOTDA**, proved most successful in photostabilizing polymer thin films, with up to 95% of the initial emission intensity retained at the end of the 30 or 60 min irradiation period. Moreover, these additives did not phase separate or evaporate from thin films, were thermally stable, and could be stored for extended periods without significant decomposition.

**Supporting Information Available:** Complete experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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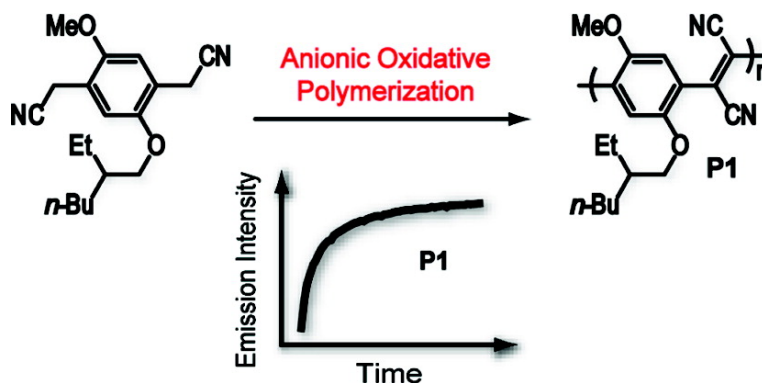
Communication

## Anionic Oxidative Polymerization: The Synthesis of Poly(phenylenedicyanovinylene) (PPCN2V)

Ryan M. Moslin, Trisha L. Andrew, Steven E. Kooi, and Timothy M. Swager

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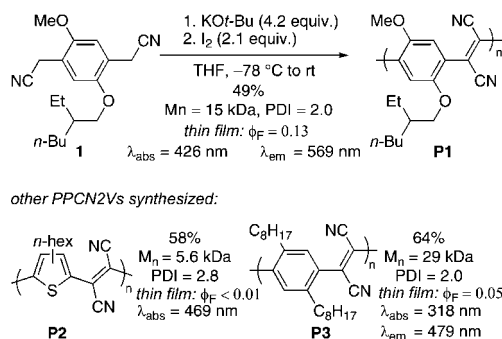
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The application of polymeric semiconductors to organic light emitting diodes,<sup>1</sup> field-effect transistors,<sup>2</sup> and photovoltaic cells<sup>3</sup> requires both p- and n-type materials. Although p-type polymers are readily available,<sup>4</sup> stable n-type polymers remain largely elusive.<sup>5</sup> Access to conjugated high electron affinity polymers remains a critical challenge within the field of polymer synthesis. One of the most successful strategies has been the construction of poly(phenylene vinylenes) (PPVs) containing cyano-substituted olefins via a polymeric Knoevenagel condensation.<sup>1,6</sup> The cyano substituents greatly increase the electron affinity, while allowing for the tuning of the polymer properties via variation of the aryl rings.

Despite the utility of the Knoevenagel polymerization, the technique cannot be adapted to form dicyano-PPVs (PPCN2Vs). Such polymers would have even greater electron affinities than the monocyano variants, but no syntheses of such systems have been described. Here we report a new polymerization technique, which provides access to PPCN2V polymers. The procedure affords higher molecular weights than the Knoevenagel polymerization and requires only a single starting material. The resulting polymers are highly photostable, easily reduced, and soluble in organic solvents.

The oxidative dimerization of phenyl acetonitrile using an alkoxide base and iodine was first communicated in 1892<sup>7</sup> and has found recent use in materials chemistry.<sup>8</sup> It had not, however, been explored in the synthesis of polymeric systems. Monomer **1**<sup>9</sup> was chosen to test the polymerization technique based on the prevalence of MEH-PPV. We found that the addition of 4 equiv of potassium *tert*-butoxide to **1** at reduced temperature, followed by the gradual addition of iodine, with concurrent warming, resulted in efficient formation of **P1** (Scheme 1). As expected cyclic voltammetry of **P1** demonstrated that it possessed a smaller reduction potential than that of the CN-MEH-PPV polymer derived from condensation polymerization.<sup>10</sup>

Scheme 1

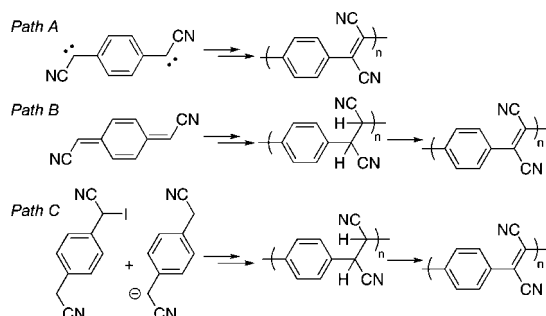


Additional monomers were also found to be compatible with this polymerization technique (Scheme 1).<sup>11</sup> Based on the interest

in poly-3-hexylthiophene (P3HT) in materials science,<sup>12</sup> the corresponding PPCN2V **P2** was generated, which also demonstrated that heterocycles are well tolerated by this polymerization technique. The low quantum yield of **P2** is consistent with the weak fluorescence of a related monocyano variant.<sup>13</sup> **P2** showed negative solvatochromism and displayed modestly higher quantum yields in nonpolar solvents,<sup>14</sup> which possibly supports the existence of a charge transfer deactivation of the excited state. Less electron-rich systems, relative to **P1**, also appear viable as shown by the synthesis of **P3**. In all cases the polymers were free of side products as determined by NMR and elemental analysis.<sup>15</sup>

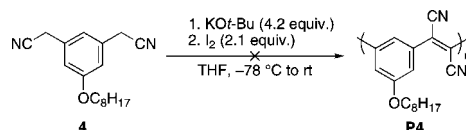
There are many potential pathways that this polymerization could be proceeding through (Scheme 2). *Path A* is distinguished from other pathways by the absence of a saturated intermediate during polymerization. By using fewer equivalents of base/oxidant, we were able to test for the existence of a saturated intermediate and in fact a copolymer featuring both saturated and unsaturated repeat units was observed. This polymer can be converted to its fully oxidized form (**P3**) by re-exposure to the polymerization conditions.

Scheme 2



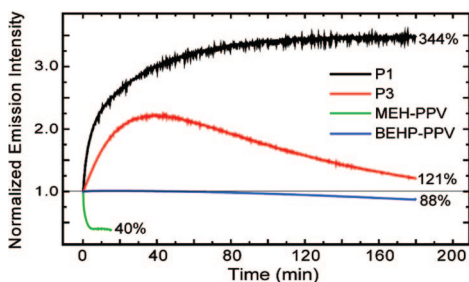
Thus, it seems reasonable to conclude that *Path A* is not operating in this polymerization.<sup>16</sup> If *Path B* is the predominant mechanism then *meta*-substituted aromatic systems are unlikely to polymerize efficiently. In comparison, in an S<sub>N</sub>2 pathway (*Path C*) as well as a carbene pathway (*Path A*) the geometric relationship between the acetonitrile substituents is irrelevant and *meta*-systems should behave similarly to the *para*-systems; this was not observed to be the case (Scheme 3). Thus, it would appear that the reaction likely proceeds most favorably through a quinoidal intermediate as with the Gilch polymerization.<sup>17</sup>

Scheme 3



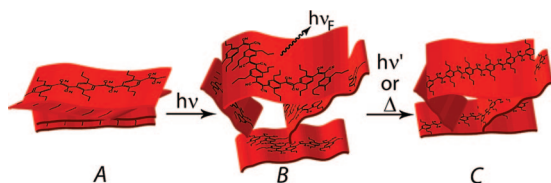


The PPCN2Vs have unusual photophysical characteristics in thin films. Prolonged irradiation<sup>18</sup> of thin films of **P1** and **P3** resulted in increased photoluminescence (Figure 1).<sup>19</sup> Placing the thin film in the dark for 48 h does not result in the quantum yield reverting to its original value; rather it matched that observed when irradiation was halted. The excellent photostability of the PPCN2Vs is exemplified by contrasting their behavior with that of MEH-PPV, which bleaches almost instantly under the same conditions, as well as BEHP-PPV, which is marketed as a photostable PPV but showed a steady decline in fluorescence after 60 min of irradiation (Figure 1). In comparison, **P3** possessed a greater quantum yield than its initial value, even after continuous excitation for 3 h. Bleaching of the even harder **P1** was not observed.



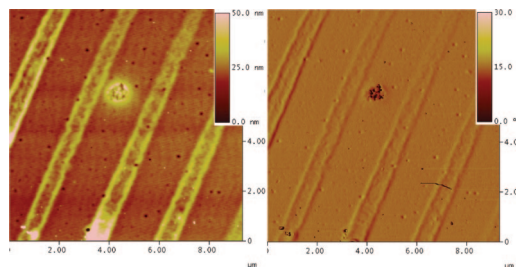
**Figure 1.** Evolution of emission intensity of thin films with continuous irradiation at maximum absorption: 426 (**P1**), 318 (**P2**), 485 (MEH-PPV), and 402 nm (BEHP-PPV).

We initially thought the observed increase in quantum yield was the result of photodegradation of a quenching impurity. However, neither extensive purification of the polymer<sup>15</sup> nor performing the irradiation under inert atmosphere altered the observed increase in quantum yield. We now favor that this unique behavior results from a *cis/trans* isomerization in some of the subunits of the polymer, as is known to occur with stilbene systems.<sup>20</sup> This is illustrated conceptually in Figure 2. In the initial, spun-cast, film (A) the polymers are closely packed and a majority of excitons are deactivated by self-quenching.<sup>21</sup> Irradiation of the thin film results in *cis/trans* isomerization of the olefins in the PPV that disrupts the tight packing due to the significant geometrical change associated with such isomerizations (B). The accompanying diminished interpolymer associations reduce quenching. Removal of the polymer from light could result in the polymers returning to their original conformer distribution (C). However, the reduced mobility of polymer chains in the film makes thermal reformation unlikely; thus the increased quantum yield persists.



**Figure 2.** *Cis/trans* isomerization as a rationale for the observed increase in quantum yield in the thin film.

Proof of the topological change proposed in Figure 2 was obtained by irradiating a thin film of **P1** at 400 nm with a laser using a parallel-line interference pattern and examining the film by atomic force microscopy (AFM) (Figure 3). The images show a pronounced increase in film thickness, ~12 nm on average,<sup>22</sup> at



**Figure 3.** AFM height (left) and phase (right) images of a 196 nm thick film of **P1** after exposure to a parallel line interference pattern (400 nm, 2 mW, 150 fs pulses, at 60 Hz for 10 s). The circular mark near the center corresponds to a film defect.

the sites of irradiation. No such effect is observed using BEHP-PPV, suggesting that the swelling is not a result of localized heating but rather is a consequence of the disruption of the packing in the thin film caused by the *cis/trans* isomerizations.

In summary, anionic oxidative polymerization represents a new means to access conducting polymers, and it has allowed for the first ever synthesis of PPCN2V systems. The polymers presented herein are extremely photostable and represent easily accessible, high electron affinity conductive polymers.

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**Supporting Information Available:** Spectroscopic information and representative experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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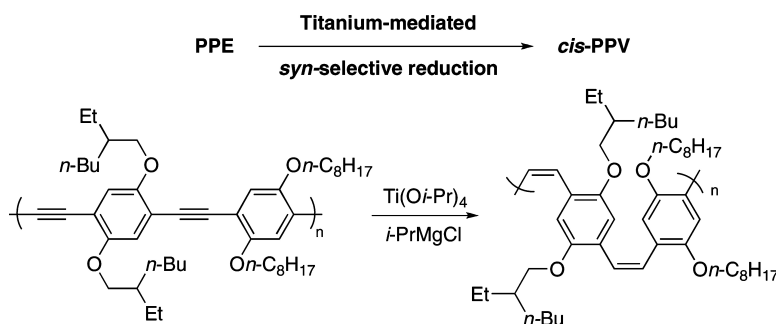
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## Synthesis of Conjugated Polymers Containing *cis*-Phenylenevinylenes by Titanium-Mediated Reductions

Ryan M. Moslin, Christine G. Espino, and Timothy M. Swager

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## Notes

# Synthesis of Conjugated Polymers Containing *cis*-Phenylenevinylenes by Titanium-Mediated Reductions

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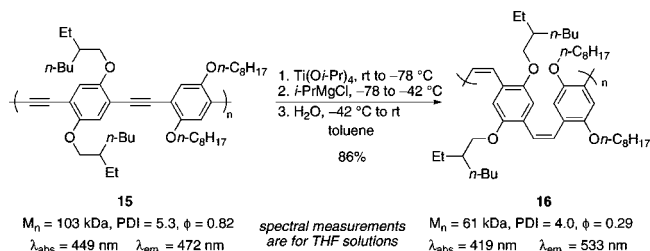
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## Introduction

Poly(phenylenevinylene)s (PPVs) are among the most actively studied conjugated polymers.<sup>2</sup> Although many techniques to synthesize high-molecular-weight PPVs exist, they are largely limited to the synthesis of predominantly *trans*-PPVs.<sup>2</sup> Recent work by Katayama and Ozawa has, for the first time, provided access to all *cis*-PPVs by way of a stereospecific Suzuki–Miyaura cross-coupling polymerization of 1,4-bis((*Z*)-2-bromovinyl)benzenes with arylbis(boronic acid)s.<sup>3</sup> We have been interested in an alternative approach where, rather than build a PPV with a preordained stereochemistry, a postpolymerization *syn*-selective reduction on a poly(phenylene ethynylene) (PPE) is employed. This scheme has the advantage that high-molecular-weight PPEs can be synthesized using either Pd catalysis or alkyne metathesis.<sup>4</sup> This route could also potentially allow for the access to an additional array of PPVs that are uniquely accessible from PPEs. The transformation of the triple bonds in PPEs and other acetylene building blocks to alkenes<sup>5</sup> has considerable potential.

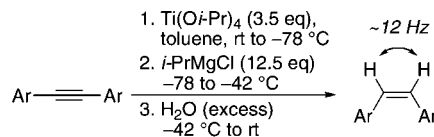
Scheme 1



Although there are many means by which to reduce alkynes to disubstituted alkenes,<sup>6</sup> we judged the titanium-mediated reduction developed by Sato to be the most promising.<sup>7</sup> This transformation is stoichiometric in both titanium and magnesium, but the reduction is quantitative and completely *cis*-selective for a wide variety of alkyne systems. Additionally, the titanium and magnesium oxide byproducts can be easily removed with an aqueous work-up, thus minimizing the amount of impurities in the polymer product.<sup>8</sup>

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Table 1. *Cis*-Selective Reduction of Alkyne Model Systems



entry	alkyne	product	yield <sup>a</sup>
1			93%
2			90%
3			76%
4			69%
5			82%
6			99%
7			66%

<sup>a</sup> Yields are for isolated material and are not necessarily good representations of overall conversion.

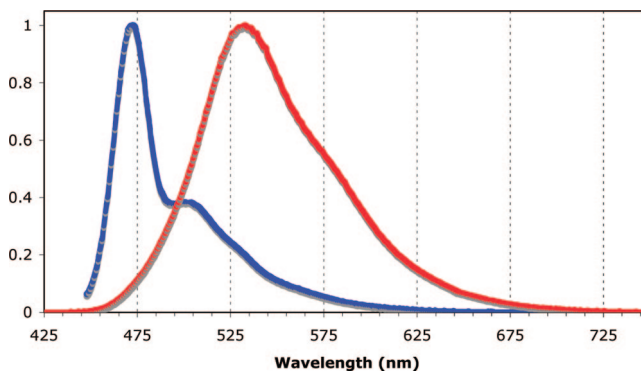
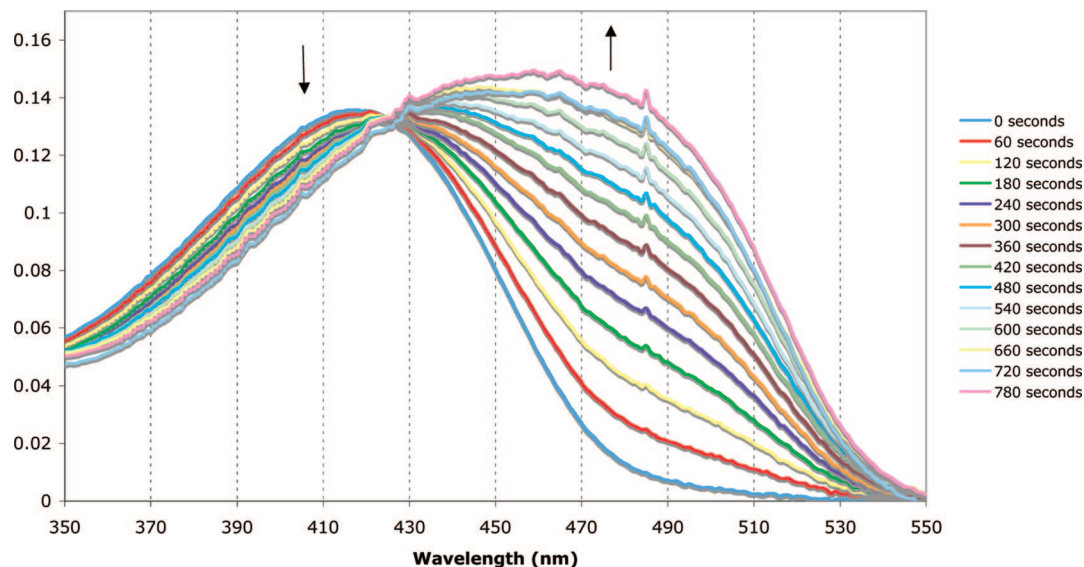
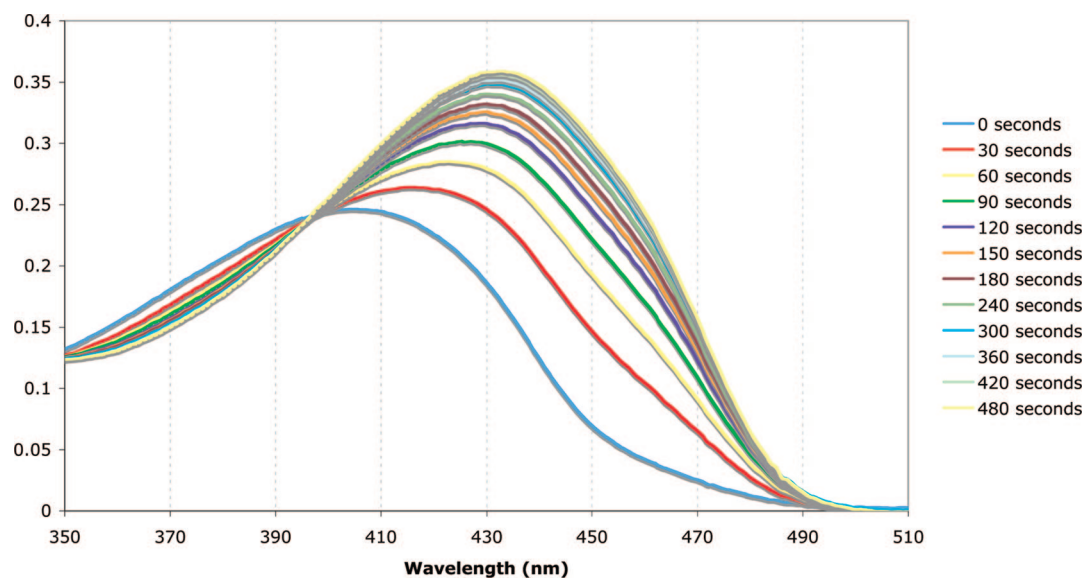


Figure 1. Overlay of normalized fluorescence spectrum of **15** (blue) and **16** (red) in THF.

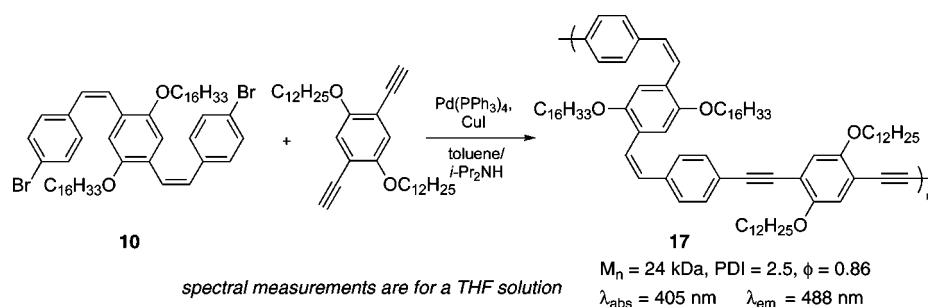


**Figure 2.** Changes in the absorption spectrum of **16** under irradiation (365 nm) in THF demonstrating a transformation from the *cis*-alkene to *trans*-alkene conformation.



**Figure 3.** Changes in the absorption spectrum of **17** under irradiation (365 nm) in THF demonstrating a *cis* to *trans* isomerization.

**Scheme 2**



## Results and Discussion

In contrast to Sato's work, diethyl ether was not a suitable solvent for these substrates. However, with toluene as the solvent, the desired *cis*-olefins are obtained in excellent yields and selectivities (entries 1 and 2, Table 1). The geometry of the olefins was assigned by the coupling constants of the vinyl protons. The reaction is tolerant of a variety of substitution

patterns, most notably the *ortho*-bromo groups of **7** (entry 5) and the *meta*-alkyne isomer (**9**, entry 6). The tetrayne **11** was also successfully reduced (entry 7), although isolation difficulties resulted in a slightly diminished yield.

The low temperature of the reaction made application to polymer systems challenging, as many PPEs are insoluble in toluene at  $-78^\circ\text{C}$ .<sup>9</sup> However, the reaction appears viable for



systems that are soluble at low temperatures. Using the standard conditions, polymer **15** was cleanly reduced to PPV **16** (Scheme 1, Figure 1).<sup>10,11</sup> The isolated polymers behaves similarly to the materials described in earlier work describing all *cis*-PPVs,<sup>2</sup> and these materials undergo an irreversible red shift in absorbance when exposed to UV light (Figure 2).

A means to effectively expand the scope of this reaction in the synthesis of polymers having *all-cis*-PPV linkages is to convert *p*-bromo-functionalized diyne systems such as **9** to the corresponding *cis*-diene and then perform a Sonogashira polymerization with a diyne to make an *all-cis*-PPV/PPE copolymer (Scheme 2). Polymer **17** shows a similar *cis*–*trans* isomerization under irradiation as **16** (Figure 3). *all-cis*-PPV/PPE copolymers should have greater availability and versatility compared to the *all-cis*-PPV accessed via the titanium-mediated reduction of PPEs.

## Conclusion

This work represents the first and only example of converting a PPE to an *all-cis*-PPV system. Although limited in polymer scope, this method does appear complementary to existing *cis*-PPV syntheses, which required lengthy monomer synthesis and did not provide an example of a PPV possessing substitution on both phenyl subunits.<sup>2</sup> Additionally, this technique provides access to potentially useful *all-cis*-monomers for use in polymer synthesis.

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**Supporting Information Available:** Spectroscopic information for all new compounds as well as representative experimental

procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) The higher molecular weight of **15**, as compared to **16**, can be potentially explained by the propensity for GPC analysis to overestimate the molecular weights of rigid polymers such as PPEs; see: Räder, H. J.; Spickermann, J.; Kreyenschmidt, M.; Müllen, K. *Macromol. Chem. Phys.* **1996**, *197*, 3285–3296.

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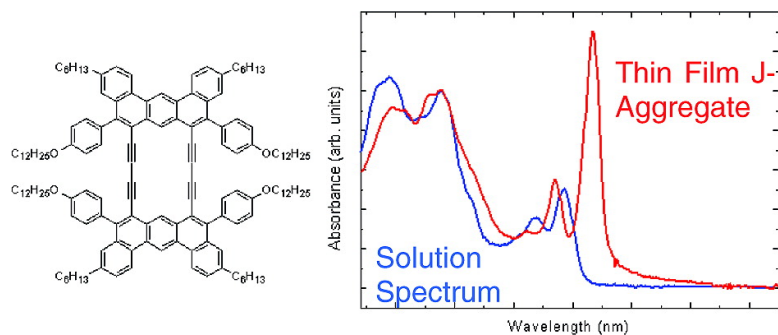
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# Synthesis of J-Aggregating Dibenz[*a*,*j*]anthracene-Based Macrocycles

Julian M. W. Chan, Jonathan R. Tischler, Steve E. Kooi, Vladimir Bulovic#, and Timothy M. Swager

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Synthesis of J-Aggregating Dibenz[a,j]anthracene-Based  
MacrocyclesJulian M. W. Chan, Jonathan R. Tischler, Steve E. Kooi, Vladimir Bulović, and  
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**Abstract:** Several fluorescent macrocycles based on 1,3-butadiyne-bridged dibenz[a,j]anthracene subunits have been synthesized via a multistep route. The synthetic strategy involved the initial construction of a functionalized dibenz[a,j]anthracene building block, subsequent installation of free alkyne groups on one side of the polycyclic aromatic framework, and a final cyclization based on a modified Glaser coupling under high-dilution conditions. Photophysical studies on three conjugated macrocycles revealed the formation of J-aggregates in thin films, as well as in concentrated solid solutions (polyisobutylene matrix), with peak absorption and emission wavelength in the range of  $\lambda = 460\text{--}480\text{ nm}$ . The characteristic red-shifting of the J-aggregate features as compared to the monomer spectra, enhancement in absorption intensities, narrowed linewidths, and minimal Stokes shift values, were all observed. We demonstrate that improvements in spectral features can be brought about by annealing the films under a solvent-saturated atmosphere, where for the best films the luminescence quantum efficiency as high as 92% was measured. This class of macrocycles represents a new category of J-aggregates that due to their high peak oscillator strength and high luminescence efficiency have the potential to be utilized in a variety of optoelectronic devices.

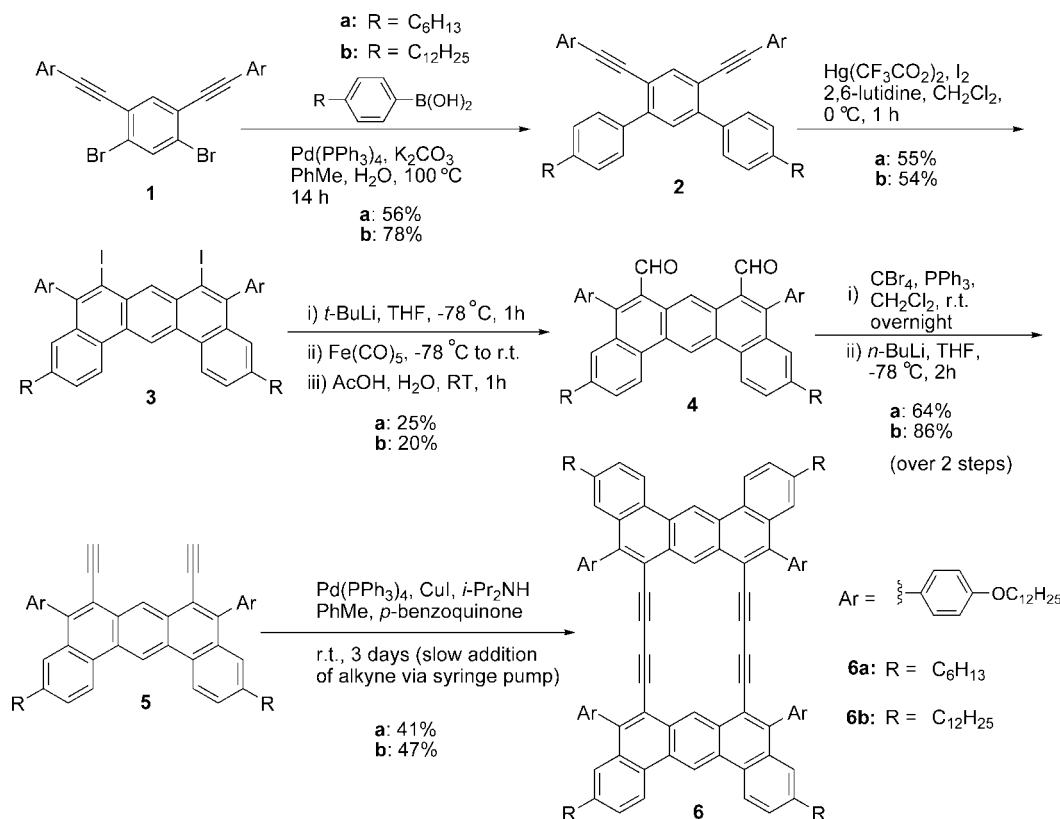
## Introduction

Shape-persistent macrocycles have received much attention in the field of materials science, particularly in the area of nanoscale architectures.<sup>1</sup> The first macrocycle featuring two unfunctionalized anthracenes linked by 1,3-butadiyne bridges was reported in 1960, but due to the lack of modern synthetic and characterization methods, the nature of the resulting material was not rigorously elucidated.<sup>2</sup> Following little interest in such systems over the next four decades, reports of anthrylene-ethynylene oligomers and macrocycles have surfaced in the past 5 years.<sup>3</sup> However, the molecular rigidity and lack of solubilizing groups resulted in the reported compounds having poor solubilities in common solvents. To create a class of molecules that could have potentially interesting photophysical and materials properties, we embarked on the design of conjugated macrocycles based on rigid dibenz[a,j]anthracene units bridged by butadiyne  $\pi$ -linkers. This was a logical choice since aryleneethynylene and 1,3-butadiyne linkages are frequently used in conjugated systems (e.g., polymers) for their ability to maintain rigidity and  $\pi$ -conjugation.<sup>4</sup> The polycyclic aromatic

motifs are commonly seen in other areas of materials science, notably in the fields of discotic liquid crystals and graphitic materials.<sup>5</sup> By employing various modern synthetic transformations, it was possible to introduce numerous functionalities (e.g., side chains) into the structure to give better solubility and processability. In particular, bulky 4-alkoxyphenyl substituents located near the middle of the macrocycles serve several purposes: (1) as synthetic handles to allow for the facile electrophilic cyclizations<sup>6</sup> used to establish the dibenz[a,j]anthracene framework, (2) as solubilizing groups, and most importantly, (3) as a source of steric hindrance to bring about twisting of the  $\pi$ -system. Such distortion of the rigid framework by steric bulk has been known to induce slipped stacking arrangements,<sup>7</sup> resulting in aggregate structures with unique optical properties. Similar slipped structures are also known in nature: for example, the arrangement of J-aggregated chlorophyll chromophores is crucial to the light-harvesting efficiency of

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Scheme 1. Synthesis of Macrocycles **6a** and **6b**

photosynthetic systems.<sup>8</sup> Using natural photosystems as a guide and inspiration, researchers have found ways to emulate this J-aggregate design in various porphyrins and perylene bisimides.<sup>9</sup> More recently, the laboratories of Frank Würthner have also successfully implemented the rational synthesis of several J-aggregated systems using supramolecular design principles.<sup>10</sup> Ever since their serendipitous discovery in 1936, J-aggregates have been of great theoretical interest because they display coherent, cooperative phenomena like superradiance and giant oscillator strength, a consequence of their electronic excitation being delocalized over several molecules.<sup>11</sup> Besides being theoretical curiosities, J-aggregates also have a myriad of practical applications, such as their use as organic photoconductors,<sup>12</sup> photopolymerization initiators,<sup>13</sup> and nonlinear optical devices,<sup>14</sup> as well as the emerging applications such as the

recently demonstrated critically coupled resonators<sup>15</sup> and strongly QED coupled microcavity LEDs.<sup>16</sup>

Herein, we report the synthesis and characterization of a series of J-aggregating macrocycles based on functionalized dibenz[*a,j*]anthracene fragments linked at the 6- and 8- positions by a pair of 1,3-butadiyne bridges, in which the ring interior can be viewed as an octadehydro[18]annulene system. The results of their photophysical studies are also detailed.

## Results and Discussion

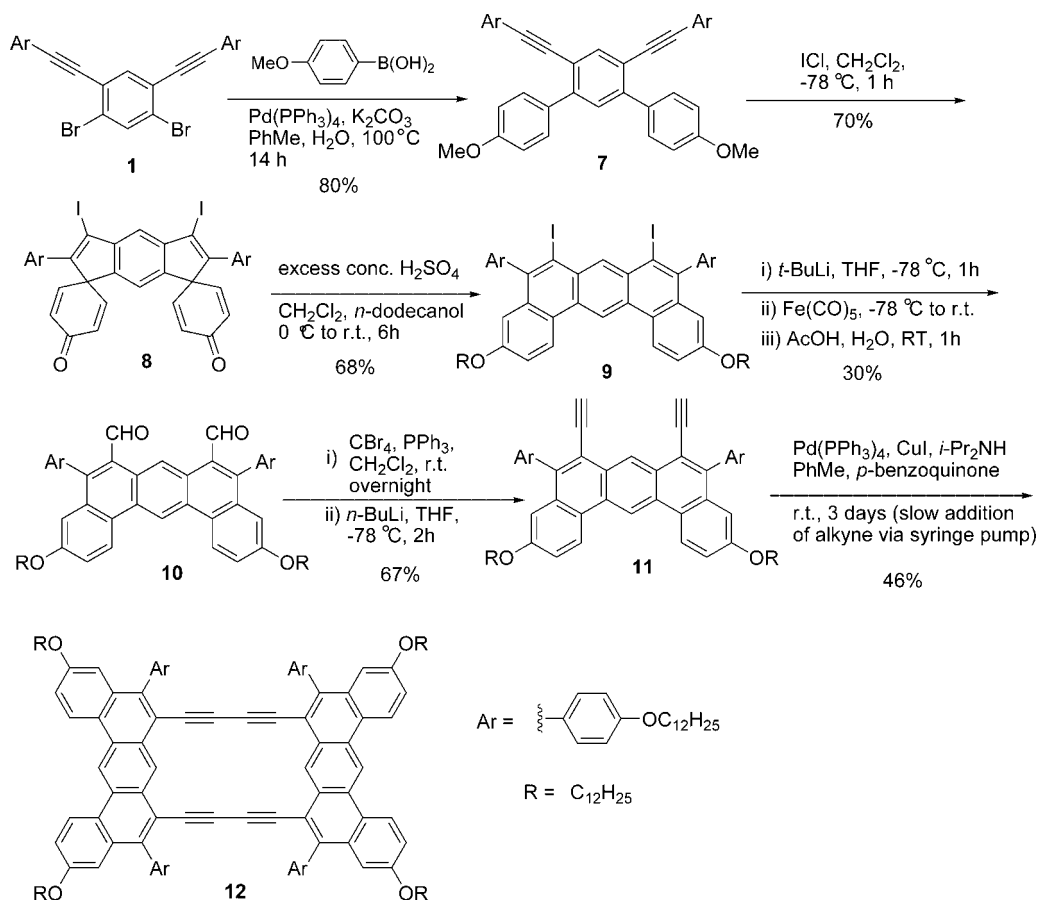
**Synthesis.** Macrocycles **6a** and **6b** were prepared in six steps from the previously reported dibromide **1**<sup>14</sup> (Scheme 1). Subjecting the dibromide to a double Suzuki coupling with 4-alkylphenylboronic acids afforded terphenyl derivatives **2**, which were then converted to the required 6,8-diiododibenz[*a,j*]anthracenes via a double iodonium-induced electrophilic cyclization.<sup>17,18</sup> Numerous attempts to convert the diiodide to the bis-acetylene **5** via Sonogashira and Castro–Stephens reactions proved unsuccessful, instead resulting in complex,

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Scheme 2. Synthesis of Macrocycle 12



undefined mixtures. However, an indirect method involving a lithiation/carbonylation sequence to give **4**, followed by Corey–Fuchs homologation,<sup>19</sup> successfully afforded dialkyne **5**. Owing to the sterically encumbered environment of the reaction centers, dialdehyde **4** was always accompanied by the formation of monoaldehyde byproduct **13**. Separation of the two could however, be easily achieved by column chromatography. Finally, an oxidative coupling utilizing conditions previously developed<sup>20</sup> in our group was performed, furnishing macrocycles **6a** and **6b** in reasonable yields.

The synthesis of macrocycle **12** (Scheme 2) involved a similar sequence of transformations employed in the preparation of **6a** and **6b**, with the exception that the bis-alkoxyterphenyl **7** could only be converted to the desired diiodide **9** in two steps, via a skeletal rearrangement of the structurally intriguing **8**, using modifications of known reactions.<sup>6,21</sup> A second alkoxy-based macrocycle bearing branched farnesol-derived side chains was also synthesized in a manner analogous to **12**, with its existence confirmed by MALDI-TOF. Unfortunately, this fourth and final macrocycle could not be satisfactorily separated from a trimeric byproduct even after repeated column chromatography and attempted fractional recrystallizations. In addition to the three macrocycles, compound **15** (the acyclic analogue of **6a**) was also prepared to study the effect of the number of bridges on

the photophysical properties. This was made in three steps (Scheme 3) starting from monoaldehyde **13**, which is a byproduct isolated during the purification of dialdehyde **4a**.

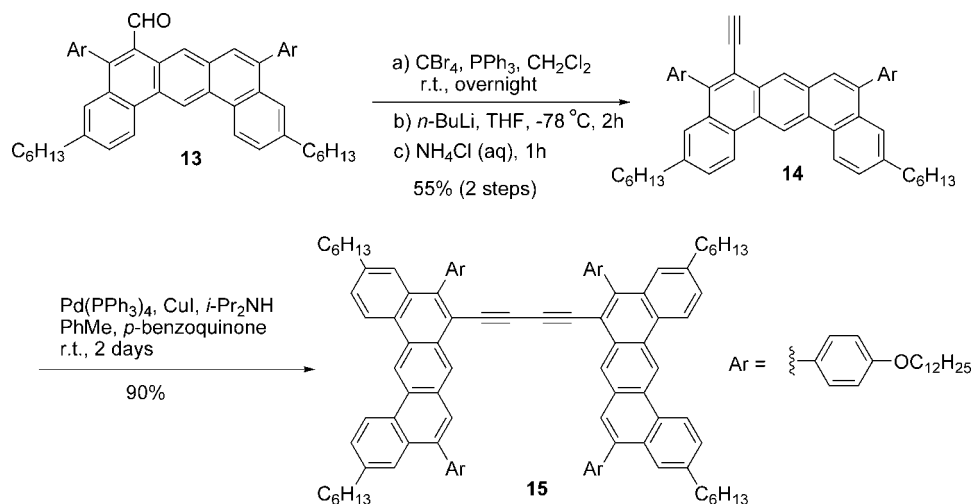
The above-mentioned target compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, high-resolution mass spectrometry (MALDI-TOF), UV–vis, and fluorescence spectroscopy. In the <sup>1</sup>H NMR spectra of the macrocycles, the two protons located within the ring were found to be shifted downfield ( $\delta \approx 9.5$  ppm) as a result of van der Waals deshielding brought about by steric interactions. The lack of any upfield shift of those internal protons implies the absence of a ring current<sup>22</sup> in these systems (i.e., no diatropic effect observed). Brief polarized optical microscopy experiments were also performed on the macrocycles in hope of finding liquid crystalline behavior as well, but the compounds had extremely high melting points (between 200 and 330 °C) and were also observed to decompose and discolor at those elevated temperatures.

**Photophysical Studies.** A SPEX fluorolog, with dual monochromators, was used to collect photoluminescence (PL) and photoluminescence excitation (PLE) spectra. The instrument is wavelength and intensity calibrated, and it compensates for variations in excitation intensity by monitoring the incident optical power level. In PL measurements, the **6a** films were optically excited at a wavelength  $\lambda = 375$  nm. For PLE spectra,

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## Scheme 3. Synthesis of Acyclic 15



emission at  $\lambda = 508$  nm was collected. Figure 1 shows the UV–vis absorption and fluorescence spectra of the four compounds in chloroform. Macrocycles **6a** and **6b** displayed essentially identical spectral profiles, with absorption and emission maxima occurring at around 440 and 455 nm, respectively. Changing the peripheral alkyl groups to alkoxy chains (e.g., **12**) resulted in a slight bathochromic shift, with the spectral shape remaining similar otherwise. The spectra of the acyclic **15** differed somewhat from the macrocycles, which was expected due to the major structural difference. Its absorption spectrum was blue-shifted relative to the others, possibly due to reduced conjugation resulting from the absence of the second diyne linker. A much larger Stokes shift was also observed, which could indicate reduced rigidity, once again as a result of having only a single linker. Fluorescence quantum yields of the compounds were measured against quinine sulfate in 0.1 N H<sub>2</sub>SO<sub>4</sub> (Table 1). The three macrocycles in chloroform solution showed fairly high quantum yields between 0.40 and 0.50, whereas the singly bridged **15** had a lower value of 0.35.

To test for the presence of J-aggregates, we investigated the thin film photophysics of the macrocycles. As **6a** was synthesized in the largest quantity, films of this compound were studied in greatest detail. The initial films were produced by spin-coating a fairly concentrated (5 mg/mL) toluene solution of **6a** on to

Table 1. Photophysical Properties of **6a**, **6b**, **12**, and **15**

compound	absorption max (nm)	emission max (nm)	quantum yield, $\Phi_F$	extinction coefficient ( $M^{-1} \text{ cm}^{-1}$ )
<b>6a</b>	443	456	0.45	90141 (at 443 nm)
<b>6b</b>	443	456	0.43	63569 (at 443 nm)
<b>12</b>	448	461	0.47	79113 (at 448 nm)
<b>15</b>	395	440	0.35	38206 (at 395 nm)

glass or quartz coverslips ( $18 \times 18 \text{ mm}^2$ ). Fortuitously, the first few films showed promising UV–vis absorption features consistent with J-aggregates (Figure 2).

Compared with the solution spectrum, the **6a** film spectrum shows an aggregate absorption peak at 467 nm (red-shifted by  $23 \pm 1$  nm from the solution). Even more notable is the high intensity and narrow line width of this peak (J-band), which dominates all other spectral features. This is in stark contrast to the solution spectrum, in which the peak at 443 nm shows much lower intensity than those between 300 and 360 nm (absorptions due to pendant *p*-alkoxyphenyl moieties). Normalizing the solution and film absorbances at 340 nm, the enhancement in the peak intensity (at 467 nm) relative to the other spectral features becomes evident (Figure 2). The bathochromic shift and the strong intensity of the aggregate peak,

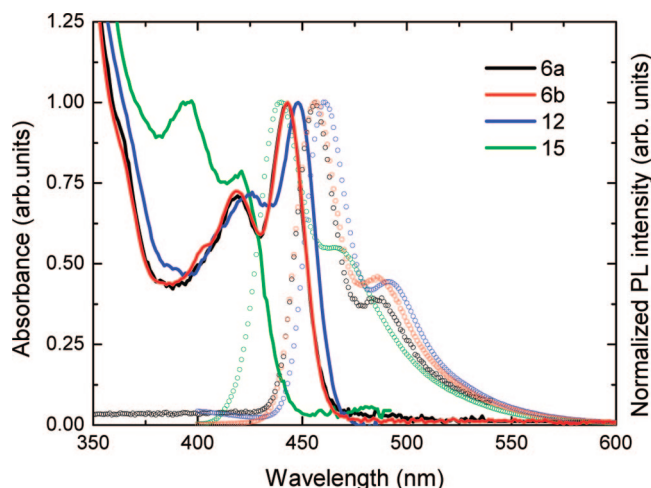


Figure 1. Normalized absorbance (solid lines) and emission (dotted lines) spectra of **6a**, **6b**, **12**, and **15** in chloroform.

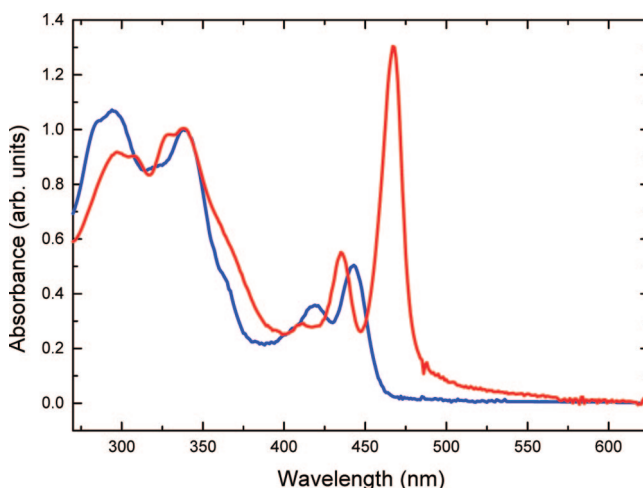
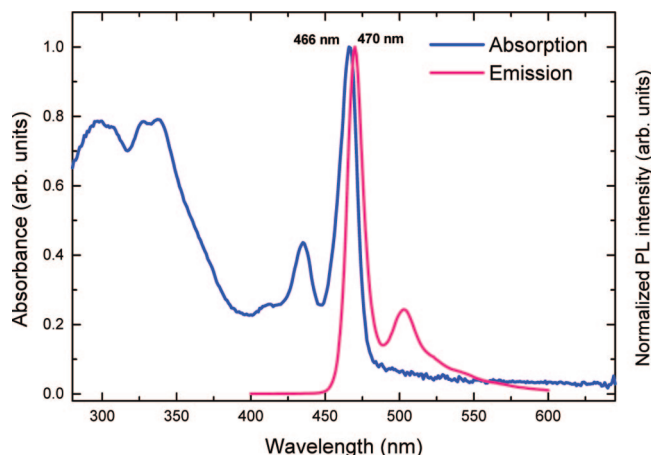


Figure 2. Absorption spectra of **6a**, solution (blue line) vs film (red line), normalized to the absorbance at 340 nm.

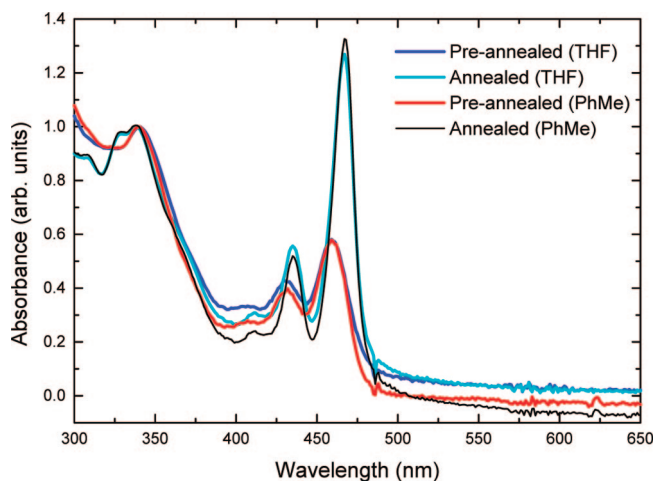


**Figure 3.** Normalized absorption (blue line) and fluorescence (pink line) spectra of **6a** (film).

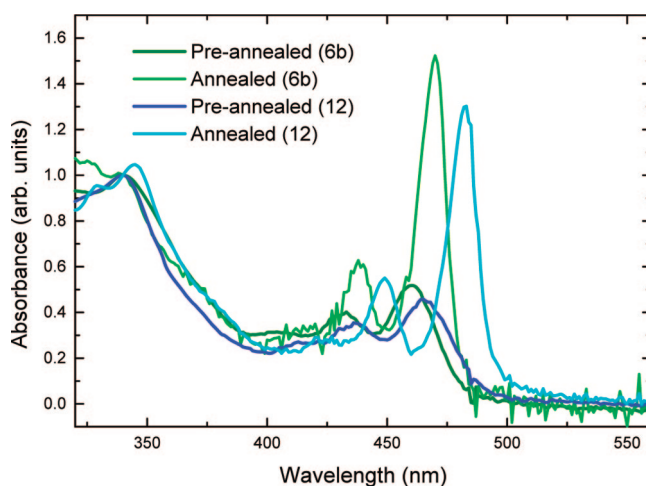
are photophysical characteristics of J-aggregates.<sup>23</sup> From the emission spectra of the **6a** films we find the Stokes shift to be only 4 nm (Figure 3), versus 13 nm in solution phase. Such minimal Stokes shift is also consistent with the existence of J-aggregates.<sup>24</sup> It is notable that the fluorescence band is a mirror image of the low-energy edge of the J-band absorption.

We also find that it is possible to spin-coat films of **6a** that did not display a J-band. These less strongly absorbing films could be produced when the spin rate (of the spin-coating process) was high (e.g., 4000 rpm), a lower concentration (<2 mg/mL) of **6a** in solvent was used, or when a more volatile solvent (e.g., THF) was employed. The use of these parameters provided for less-than-favorable conditions for aggregate formation. However, when these ‘nonaggregated’ (i.e., monomeric) films were then subjected to conditions conducive to aggregate formation, the typical J-aggregate spectral features were found to emerge with time. This was achieved by vapor-annealing the films in a solvent chamber saturated with toluene vapor for 45 min, and then retrieving them for spectral (UV–vis) reacquisition. It can be seen (Figure 4) that the vapor-annealing, which should result in more ordered thin films,<sup>25</sup> precipitates the appearance of the highly intense J-band, confirming that molecular organization was indeed important in producing the desired J-aggregate photophysics. When the volatile THF is used as the spin-casting solvent (particularly with low **6a** concentration) the resulting films lacked J-aggregate features. However, J-aggregate features can be recovered when these films are placed in a solvent chamber containing THF vapor (Figure 4).

Similar photophysical experiments were also performed on films of the two longer-chained macrocyclic analogues **6b** and **12**. In both cases, the films are cast from THF solutions of the macrocycles and subsequently annealed under THF vapor for 45 min. UV–vis data are acquired before and after the annealing process, and the spectra of **6b** and **12** are shown in Figure 5. The spectra of the preannealed films did not show J-bands, but these appeared in both cases upon annealing. Therefore, the results obtained with **6b** and **12** were analogous to those of **6a**, suggesting that the doubling of chain length of the peripheral



**Figure 4.** Absorption spectra of **6a** (film) before and after annealing under toluene (PhMe) and THF vapor, normalized to the absorbance at 340 nm.



**Figure 5.** Absorption spectra of **6b** (film) and **12** (film) before and after annealing under THF vapor, normalized to the absorbance at 340 nm.

alkyl/alkoxy groups had little effect on the photophysics, be it in solution or in the film-state. Similar J-aggregate photophysics could not be observed with the noncyclic **15**, implying that the aggregate formation may require approximate molecular planarity (steric hindrance in the noncyclic **15** produces a larger deviation from planarity, since the two dibenzanthracene subunits are less constrained). It is likely that J-aggregation of these polycyclic aromatics in the solid-state relies on  $\pi$ – $\pi$  stacking interactions that could be disrupted if the nonplanarity became too pronounced.

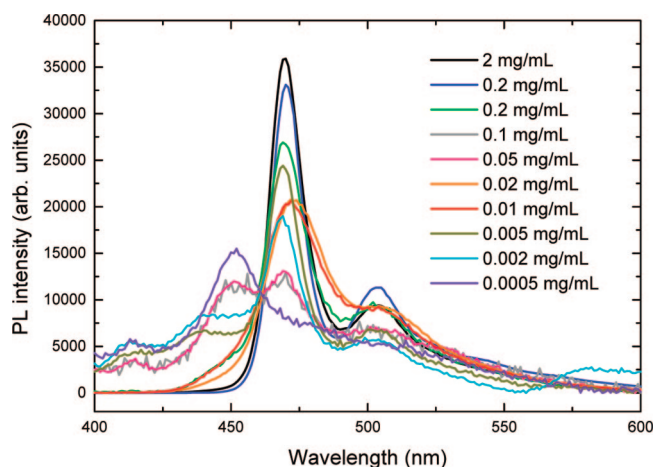
Additional experiments examining the photophysics of **6a** as a function of concentration were also undertaken. A series of films were spin-coated using **6a** solutions (polyisobutylene matrix/chlorobenzene as solvent) of varying concentrations, and their photoluminescence spectra, excitation spectra, and fluorescence lifetimes were measured. Chlorobenzene was chosen as it provided for optimal comiscibility of **6a**, polyisobutylene, and solvent. When a film containing a very low concentration of **6a** (i.e., 0.0005 mg in a 1 mL solution of 40 mg/mL polyisobutylene (PIB) in chlorobenzene) was used, its emission peak was at 455 nm (Figure 6), identical to that observed in solution spectra. As the amount of **6a** used in the spin-coating process was increased to 0.002 mg/mL of PIB/chlorobenzene,

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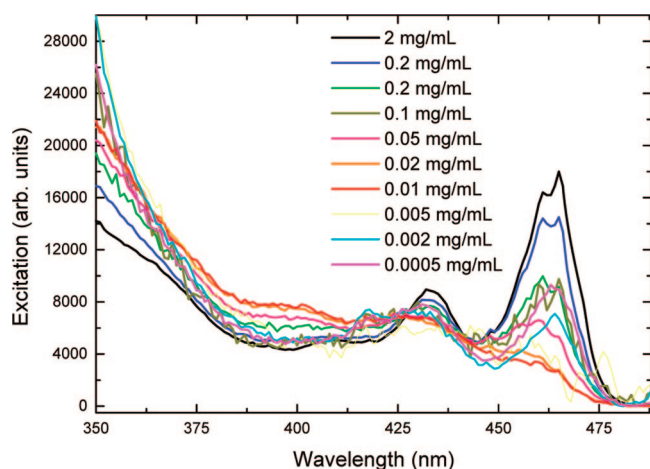
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**Figure 6.** Photoluminescence intensity vs concentration of **6a** in thin films (PL scaled by subtracting the background and scaling by integrated intensity at all wavelengths).



**Figure 7.** Excitation vs concentration of **6a** in thin films (PLE scaled by subtracting background and scaling by integrated intensity at all wavelengths).

aggregate peaks began to emerge at 470 nm with a shoulder at 500 nm, while the 455 nm “monomer” peak diminished. A further increase in **6a** concentration to 0.005 mg/mL resulted in further reduction in the 455 nm peak, so that at 0.02 mg/mL the monomer peak can no longer be observed, at which point the emission spectrum begins to resemble those obtained with neat films discussed above (pure **6a**, no PIB matrix). From the excitation spectra (Figure 7), no J-band at 470 nm could be observed at the lowest concentration of 0.0005 mg/mL, but as the concentration was increased 10-fold, a peak at 470 nm appeared, becoming more pronounced with increasing **6a** concentrations. Fluorescence lifetimes (at 470 nm) for a series of solutions and films of different concentrations were also measured. Solution lifetimes were found to be  $1.7 \pm 0.1$  ns regardless of concentration. In the film state, it can be observed from Table 2 that the lifetimes generally decrease as the concentration of **6a** was increased from 0.0005 to 2.000 mg/mL (only a small incidence of scatter is observed in the trends). In particular, with a concentration of 0.0005 mg/mL, a lifetime of  $\tau_m = 1.3$  ns was obtained, comparable to what was observed in chlorobenzene solutions, while at higher concentrations, lifetimes of about  $\tau_J = 0.24$  ns are observed. Higher doping concentration also leads to a measurable increase in thin film photoluminescence (PL) quantum yield (QY) from  $\Phi_m = 43\%$

**Table 2.** Fluorescence Lifetimes of **6a** (Solutions and Films) at Different Concentrations

concentration (mg/mL)	lifetimes (bimodal) (ns)		state
0.002	1.7 (100%)	—	solution (PhCl)
0.02	1.7 (100%)	—	solution (PhCl)
0.2	1.8 (100%)	—	solution (PhCl)
0.0005	1.3 (99.9%)	4.8 (0.1%)	film
0.002	0.2 (96.7%)	1.3 (3.3%)	film
0.005	0.3 (96.6%)	1.2 (3.4%)	film
0.01	0.3 (97.4%)	1.0 (2.6%)	film
0.02	0.2 (98.1%)	1.1 (1.9%)	film
0.05	0.6 (84.5%)	1.5 (15.5%)	film
0.10	0.4 (82.7%)	1.4 (17.3%)	film
0.20	0.4 (94.9%)	1.4 (5.1%)	film
2.00	0.2 (97.4%)	0.7 (2.6%)	film

$\pm 6\%$  for the monomeric film to  $\Phi_J = 92\% \pm 8\%$  for the aggregate films. To determine PL QY, we compared the PL counts from the **6a** film to a thin film standard of known QY, accounting for relative differences in absorption strength of the films. The standard was a thin film of thickness 75 nm of the small molecule tris-(8-hydroxyquinolino)aluminum (Alq<sub>3</sub>). The Alq<sub>3</sub> film was prepared by thermally evaporating recrystallized Alq<sub>3</sub> in ultra high vacuum (growth pressure below  $10^{-6}$  Torr) onto a quartz substrate that was carefully solvent cleaned and oxygen plasma treated to remove trace impurities. The published QY for Alq<sub>3</sub> in thin film is  $32\% \pm 2\%$ .<sup>26</sup> We erred on the side of caution and used a value of QY = 30% for our calculations. To make a fair comparison of QY, for each film in consideration, the percentage of absorbed optical excitation was determined from optical transmission measurements. Measured PL counts were then normalized to the percent absorption values, on a film by film basis. For **6a** in monomeric form, we calculated the PL QY to be  $43\% \pm 6\%$ , which is similar to the QY for **6a** in solution, and for **6a** at high doping concentrations, we determined the QY to be  $92\% \pm 8\%$ .

The emergence of a red-shifted narrower line width optical transition at higher **6a** concentrations, the corresponding reduction in lifetime, and increase in quantum yield of aggregates as compared to monomers are indicative of J-aggregate formation.<sup>27</sup> In J-aggregates, strong coupling between the monomer transition dipoles produces a new cooperative molecular state. The coupling results in a new optical transition called the J-band, when the interaction strength exceeds the monomeric dephasing processes.<sup>28</sup> The interaction between monomeric transition dipoles lowers the overall energy of the cooperative state; hence, the J-band absorption/fluorescence is red-shifted relative to that of the monomer. In the J-aggregate state, multiple molecules coherently couple, the number being denoted by  $N_c$ , and the J-aggregate exciton delocalizes over all of them.<sup>29</sup> Coherent coupling among the  $N_c$  molecules leads to the acceleration of the radiative rate of the J-band states by a factor of  $N_c$  relative to the monomer,<sup>30</sup> which translates into shorter excited-state lifetime and higher PL QY. The radiative rate enhancement is typically referred to as a superradiance phenomenon since it is

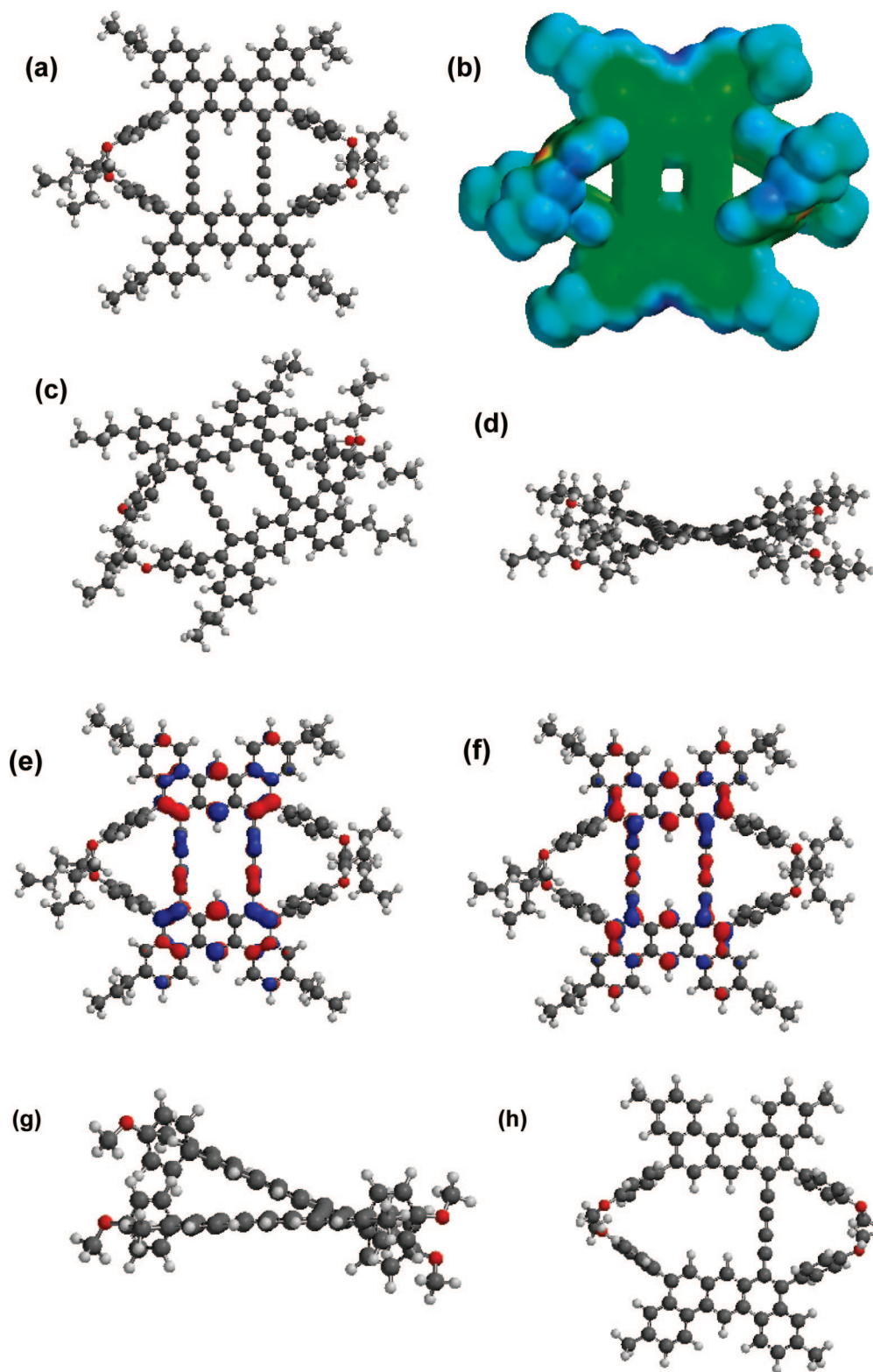
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**Figure 8.** PM3-calculated models (a) top-down view of geometry-optimized macrocyclic structure, (b) molecular electrostatic potential map, (c) optimized structure tilted to emphasize steric crowding, (d) edge-on view of optimized structure, (e) frontier HOMO, (f) frontier LUMO, (g) edge-on view of the acyclic model structure, (h) and top-down view of the acyclic structure.

caused by coherent exciton coupling,<sup>31</sup> though in J-aggregates the mechanism for the coupling is near-field Coulombic interactions while in classic superradiant systems, the origin is interference effects in the spontaneous light emission process.<sup>32</sup> Since the radiative rate of a J-aggregate increases relative to that of the monomer by a factor of  $N_c$ , from a comparison of

lifetimes ( $\tau_J$  vs  $\tau_m$ ) and quantum yields ( $\Phi_J$  vs  $\Phi_m$ ),  $N_c$  can be determined using the equation:<sup>33</sup>

$$N_c = \frac{\tau_m \Phi_J}{\tau_J \Phi_m}$$

The data obtained suggest that  $N_c$  is on the order of 12 for our **6a** J-aggregate films. Coherent coupling also leads to a narrower total line width for the J-aggregate optical transition relative to the monomer because the delocalized exciton averages out site-to-site variations and suppresses the inhomogeneous broadening.<sup>34</sup> The linewidths of the monomer optical transition and the J-band are dominated by inhomogeneous broadening. Nevertheless, the width of the J-band relative to the monomer spectrum does characterize the coherence of the system. The line width of the J-band is narrower than the monomer optical transition because in the J-aggregate state, the exciton is delocalized over the  $N_c$  molecules that are coherently coupled, which tends to average out site-to-site inhomogeneities in the exciton energy. This motional narrowing is manifest in the smaller line width for J-aggregate absorption and emission spectra. This coherent coupling also results in the accelerated radiative process in the J-aggregate state, which translates into the higher observed QY and shorter exciton lifetime for the J-aggregate compared to the monomer.

**Molecular Modeling.** In order to better visualize the equilibrium geometry of the macrocycles **6a**, **6b**, and **12**, molecular calculations<sup>35</sup> were performed at the semiempirical PM3 level, using a model compound (Figure 8) with deliberately shortened alkyl side chains to enable more rapid completion of the calculation. As can be seen in Figure 8, the macrocycle is composed of two 1,3-butadiyne-linked planar dibenz[*a,j*]an-

thracene subunits that are slightly staggered relative to each other as a result of steric crowding in the middle of the molecule. Despite this structural distortion, the core of the macrocycle retains some overall planarity, which would still allow for intermolecular  $\pi$ - $\pi$  stacking interactions. By comparison, the acyclic analog shows greater nonplanarity (Figure 8g), since the two nonrestrained aromatic subunits have more freedom to minimize steric repulsions. As a result,  $\pi$ - $\pi$  stacking interactions in acyclic **15** may be weakened.

## Conclusion

In summary, three dibenz[*a,j*]anthracene-based macrocycles have been synthesized and spectroscopically characterized. The conjugated macrocycles display pronounced photophysical properties in the solid state, such as the intense red-shifted absorbances, narrow linewidths, and small Stokes shifts, indicating J-aggregate formation. These new compounds may have the potential to be utilized in various optoelectronic devices (e.g., lasers, photovoltaics, and polaritonic devices<sup>16a,36</sup>).

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**Supporting Information Available:** Full experimental details pertaining to the synthesis of all new compounds described herein. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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# The Synthesis of Azaperylene-9,10-dicarboximides

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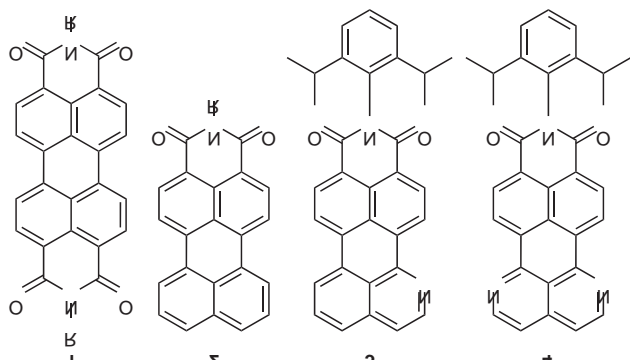
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**Abstract:** The syntheses of two azaperylene 9,10-dicarboximides are presented. 1-Aza- and 1,6-diazaperylene 9,10-dicarboximides containing a 2,6-diisopropylphenyl substituent at the *N*-imide position were synthesized in two steps starting from naphthalene and isoquinoline derivatives.

**Key words:** perylenes, isoquinolines, cross-coupling, cyclization, oxidation

Boasting brilliant colors, large extinction coefficients, near-unity fluorescence quantum yields, and remarkable photostability, perylene-based chromophores have found unique prominence as dyes and pigments.<sup>1</sup> Particularly, perylene-3,4,9,10-tetracarboxdiimides (PDI, **1**, Figure 1) are suitable for demanding applications, such as photovoltaic devices,<sup>2</sup> dye lasers,<sup>3</sup> light-emitting diodes,<sup>4</sup> and molecular switches.<sup>5</sup> The related perylene-3,4-dicarboximides (PI, **2**) can be monofunctionalized more readily than **1**,<sup>6</sup> which is interesting for certain applications, such as fluorescence labeling and controlled conjugation to other fluorophores.



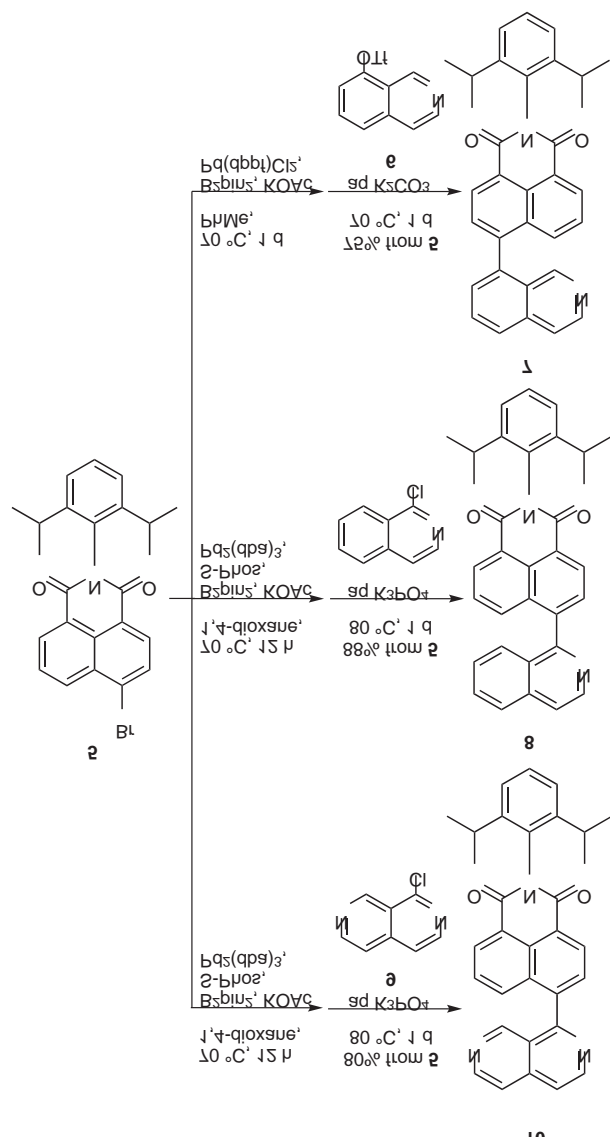
**Figure 1** Structures of PDI, PI, and azaperylene imides

Although most of the aforementioned applications capitalize on the high fluorescence efficiencies of **1** and **2**, access to the PDI or PI triplet state represents a desirable goal for some niche applications, such as solar energy conversion,<sup>7</sup> and as a method to generate deep red and/or near IR phosphorescence. Previous attempts to directly attach late transition metals to the perylene skeleton resulted in minimal electronic interaction between the metal center and PDI  $\pi$ -system.<sup>8</sup> Moreover, it was found that introduc-

ing conjugated spacers between the metal center and PDI  $\pi$ -system only yielded nonemissive complexes.<sup>7</sup> Inspired by the superior photophysical properties and high phosphorescence quantum yields of cyclometalated platinum(II), and ruthenium(II)–iridium(III) complexes,<sup>9</sup> we sought to synthesize PDI or PI analogues that contained a 2-phenylpyridine moiety that would eventually allow access to cyclometalated perylene complexes.

Along these lines, 1-azaperylene was previously synthesized and reported to undergo directed C–H activation to yield bay-functionalized 12-hydroxy-1-azaperylene, which displayed excited state intramolecular proton transfer (ESIPT).<sup>10</sup> However, due to the lack of notable functional groups in the perylene skeleton, a harsh anion-radical cyclization of either 1- or 8-( $\alpha$ -naphthyl)isoquinoline was necessary to generate the 1-azaperylene chromophore. Moreover, we anticipated that the rigidity of 1-azaperylene, combined with its lack of solubilizing groups, would lead to complexes of poor solubility. Instead, we envisioned that (a) introduction of an electron-withdrawing imide moiety to the azaperylene skeleton would allow the use of a comparatively mild, base-promoted cyclization procedure<sup>11,12</sup> to synthesize the desired azaperylene imides and that (b) introduction of bulky substituents at the *N*-imide position would greatly improve the solubility of the chromophore. Additionally, the resulting azaperylene imide chromophore would have bathochromically shifted absorption and emission spectra relative to the cyan-emitting 1-azaperylene.

Initially, a one-step synthesis of 1-azaperylene-9,10-dicarboximide (**3**) by base-promoted heterocoupling of naphthalene-1,8-dicarboximide and 1-chloroisoquinoline was attempted, based on the previously reported one-pot synthesis of terrylene diimides.<sup>12</sup> However, only homocoupling between naphthalene-1,8-dicarboximide reactants was observed and *N,N'*-bis(2,6-diisopropylphenyl) PDI was isolated in 80% yield. Therefore, a multistep approach to **3** and **4** was pursued. Precursors **7**, **8**, and **10** were synthesized by a one-pot Suzuki–Miyaura cross-coupling between a 4-bromonaphthalene-1,8-dicarboximide<sup>13</sup> and either an isoquinoline derivative<sup>14</sup> or a 2,7-naphthyridine derivative.<sup>15</sup> The boronic ester derivative of bromide **5** was generated in situ by standard palladium-catalyzed reaction with bis(pinacolato)diboron. Subsequent addition of the corresponding isoquinoline or 2,7-naphthyridine coupling partner furnished precursors **7**, **8**, and **10** in good to high yield (Scheme 1). The use of S-Phos was necessary in the cross-coupling reactions involving 1-chloroisoquinoline and 1-chloro-2,7-naphthyri-



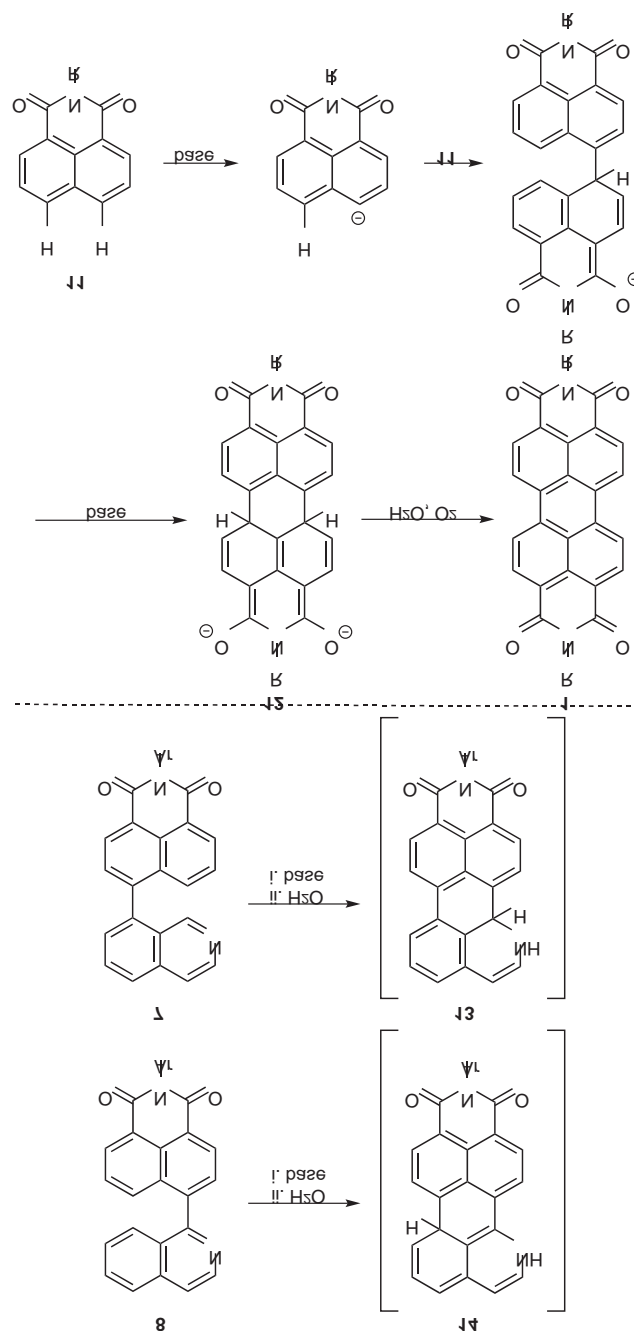
**Scheme 1** Synthesis of precursors **7**, **8**, and **10**

dine (**9**), as other phosphine ligands afforded low product yields and resulted in extensive protodehalogenation.

In order to cyclize **7**, **8**, and **10**, the base-promoted cyclization procedures described in the syntheses of extended rylene diimide chromophores were investigated.<sup>11,12</sup> In these examples, it is thought that nucleophilic attack of an arylide anion initially generates the leuco form of the chromophore **12**, which subsequently oxidizes to form the rylene skeleton (Scheme 2).<sup>16</sup> Compounds **7** and **8**, which are both precursors to azaperylene imide **3**, differ only in the position at which the naphthalene imide and isoquinoline rings are linked. We anticipated (a) that these isomeric structures would display different amenabilities to the initial arylide attack and (b) that the resulting isomeric leuco forms of **3** would display varying stabilities to oxidation.

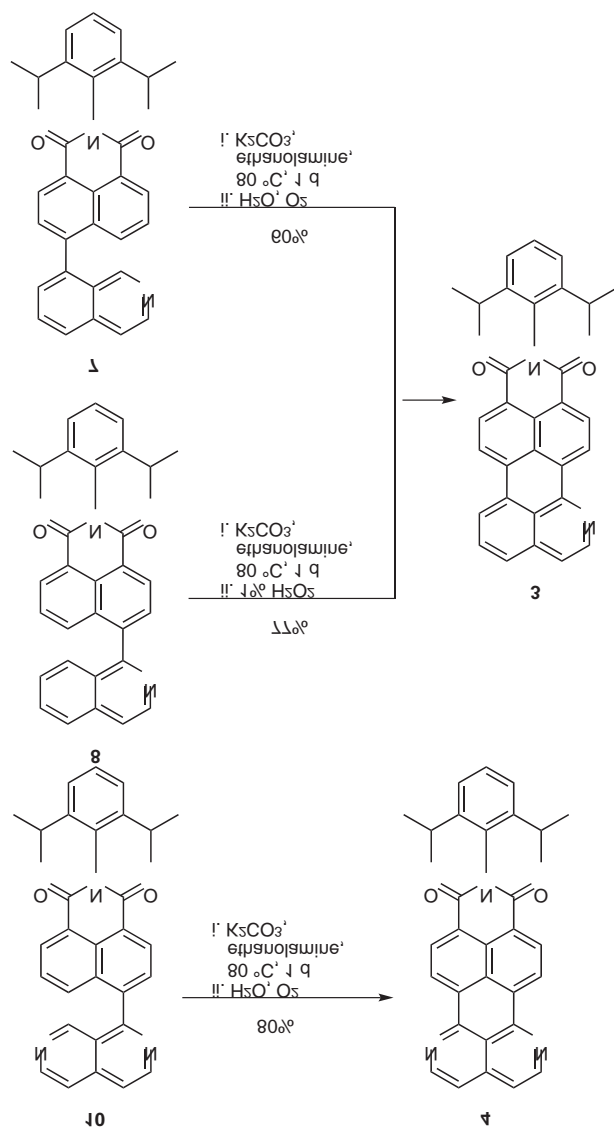
Treatment of **7**, **8**, and **10** with  $K_2CO_3$ /ethanolamine and subsequent heating initially resulted in the formation of the reduced versions of the desired azaperylene imide

chromophores, which upon workup and oxidation formed the desired products (Scheme 3). The individual reduced forms of **3** and **4** generally displayed a greater resistance to oxidation relative to their all-carbon perylene analogues. For the base-promoted cyclization reactions of **7** and **10**, stirring under air after a water workup yielded **3** and **4**, respectively, after approximately one hour. In the case of precursor **8**, however, the yield of **3** was improved if the workup procedure included hydrogen peroxide. Based on this observation, we posit that leuco compound **14** is slightly more stable compared to leuco compound **13**. Unfortunately, attempts to isolate and purify the various reduced forms of **3** and **4** were unsuccessful, as the



**Scheme 2** Base-promoted cyclization of rylene imides



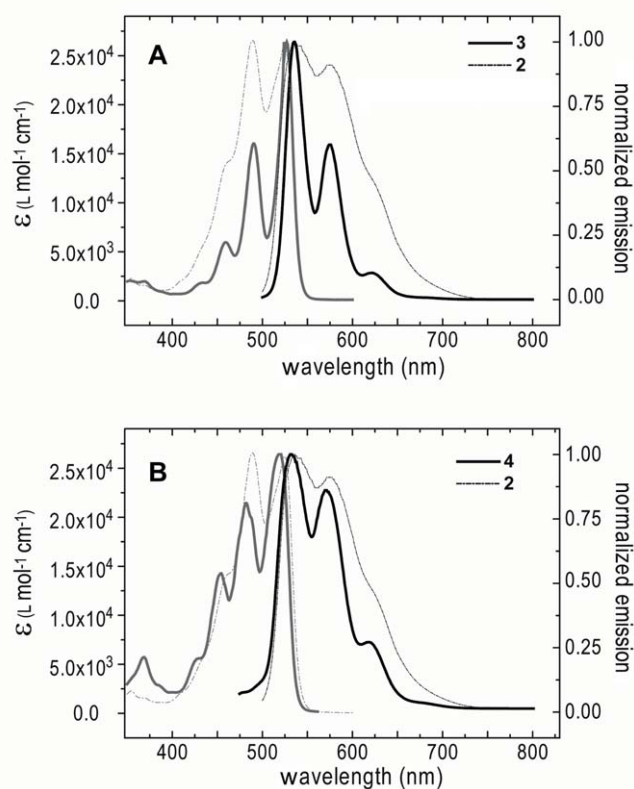


**Scheme 3** Base-promoted cyclization to synthesize **3** and **4**

azaperylene imides were inevitably obtained in most trials.

Azaperylene imide **3** was very soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , MeOH, EtOH, and MeCN while **4** was very soluble in MeOH and MeCN and only partially soluble in  $\text{CHCl}_2$  and  $\text{CHCl}_3$ . The absorption and emission spectra of **3** and **4** are shown in Figure 2. Both azaperylene imides display similar absorption and emission bands to the carbon analogue **2** ( $\text{R} = 2,6$ -diisopropylphenyl). The fluorescence quantum yield is 93% for both **3** and **4**, compared to ca. 98% for **2**. Additionally, the fluorescence lifetimes of all three chromophores were also similar: 4.71 ns for **2**, 4.82 ns for **3**, and 4.94 ns for **4**.

In conclusion, azaperylene imide and diazaperylene imide were synthesized in two steps starting from naphthalene imide and either an isoquinoline derivative or a 2,7-naphthyridine derivative. Base-promoted cyclization of binaphthoid intermediates resulted in reduced versions of the desired chromophores, which had a finite lifetime and



**Figure 2** Absorption (grey) and emission (black) spectra of (A) **3** and (B) **4** in chloroform; the absorption and emission spectra of the carbon analogue **2** ( $\text{R} = 2,6$ -diisopropylphenyl) is also superimposed (dotted line)

could be oxidized to yield 1-aza- and 1,6-diaza perylene-9,10-dicarboximides. The azaperylene imides display similar photophysical characteristics to their carbon analogues. Studies into the cyclometalation of these chromophores are currently under way.

**Supporting Information** for this article is available online at <http://www.thieme-connect.com/ejournals/toc/synlett>.

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**Thermally-Polymerized Rylene Nanoparticles**

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# THERMALLY-POLYMERIZED RYLENE NANOPARTICLES

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**ABSTRACT.** RYLENE DYES FUNCTIONALIZED WITH VARYING NUMBERS OF PHENYL TRIFLUOROMETHYL  
MOIETIES WERE SUBJECTED TO A THERMAL EMULSION POLYMERIZATION TO YIELD SHAPE-PE  
CHROMOPHORE NANOPARTICLES. PERYLENE AND TERRYLENE DIIMIDE DERIVATIVES CONTAINING  
PHENYL TFVE FUNCTIONAL GROUPS WERE SYNTHESIZED AND SUBJECTED TO THERMAL EMULSION  
POLYMERIZATION IN TETRAHYDROFUR. DYNAMIC LIGHT SCATTERING MEASUREMENTS INDICATED THAT PARTICLES WITH  
DIAMETERS OF 100 NM WERE OBTAINED IN TETRAHYDROFUR, DEPENDING ON MONOMER CONCENTRATION. THE  
PHYSICAL PROPERTIES OF INDIVIDUAL MONOMERS WERE PRESERVED IN THE NANOEMULSIONS AND EMULSIONS  
COULD BE TUNED BETWEEN YELLOW, ORANGE, RED, AND DEEP RED. THE NANOPARTICLES WERE FOUND TO  
DISSOLVE UPON DISSOLUTION INTO WATER AND THE RESULTING WATER SUSPENSIONS DISPLAYED MODEST  
QUANTUM YIELD.

## Introduction

CHROMOPHORE AND CONJUGATED POLYMER (CP) NANOPARTICLES HAVE RECEIVED SIGNIFICANT PROMINENCE IN VARIOUS APPLICATIONS, INCLUDING OPTOELECTRONICS, IMAGING AND SENSING. CERTAIN CASES, CP NANOPARTICLES DISPLAYED DESIRABLE PROPERTIES THAT WERE EITHER MORE OR NOT AS PROMINENT (TWO-PHOTON ABSORPTION CROSS SECTION) IN CP THIN FILMS OR SOLUTIONS. THERE IS CONSIDERABLE INTEREST IN USING CP NANOPARTICLES TO IMPROVE OR CONTROL THE PROPERTIES OF CP BLENDS TO IMPROVE THE EFFICIENCY OF POLYMER LEDs<sup>2,5</sup> AND PHOTONIC ENERGY TRANSFER IN SMALL MOLECULE CHROMOPHORE-CONTAINING NANOPARTICLES HAS ALSO BEEN REPORTED FOR IMAGING.<sup>3,5,6</sup>

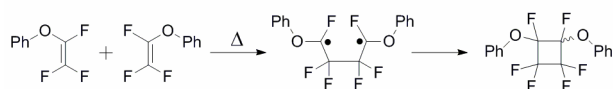
CP NANOPARTICLES ARE PREDOMINANTLY FABRICATED BY MICROPRECIPITATION METHODS. A SOLUTION OF A DILUTE SOLUTION OF THE CP IN A GOOD SOLVENT (SUCH AS TETRAHYDROFURAN) IS ADDED TO WATER WITH SONICATION. IN THE CASE OF SMALL MOLECULE CHROMOPHORES, EMULSIONS OF THE CHROMOPHORE CONTAINING POLYMERIZABLE FUNCTIONAL GROUPS ARE FIRST FORMED (SOMETIMES IN THE PRESENCE OF A METAL CATALYST) AND THEN THE MONOMERS ARE POLYMERIZED WITHIN THE MICROCAPSULES (USING EITHER A METAL CATALYSTS) TO YIELD SHAPE-PERSISTENT CHROMOPHORE-CONTAINING NANOPARTICLES. EARLY REPORTS ON 3,4,9,10-PERYLENE TETRACARBOXIDIIMIDES (PDIS), ARE FREQUENTLY USED AS THE CHROMOPHORE DUE TO THEIR BRILLIANT COLORS, LARGE EXTINCTION COEFFICIENTS, NEAR-UNITY FLUORESCENCE QUANTUM YIELDS, AND REMARKABLE PHOTOSTABILITY. RECENTLY, EXAMPLES OF RYLENE-CONTAINING NANOPARTICLES ALMOST EXCLUSIVELY BASED ON METHACRYLATE-FUNCTIONALIZED CHROMOPHORES, WHICH ARE THEN POLYMERIZED IN AQUEOUS MEDIA, HAVE BEEN ESTABLISHED CONTROLLED RADICAL POLYMERIZATION PROCESSES.<sup>3,6,7</sup>

ARYL TRIFLUOROVINYL ETHERS (TFVES) ARE A UNIQUE CLASS OF MOLECULES THAT HAVE BEEN REPORTED TO UNDERGO THERMAL DIMERIZATION REACTION TO GENERATE PERFLUOROCYCLOBUTANE (PFCB) DERIVATIVES. AND COWORKERS HAVE SYNTHESIZED NUMEROUS, HIGH MOLECULAR-WEIGHT POLYMERS BY THE POLYMERIZATION OF MONOMERS CONTAINING MULTIPLE TFVE MOIETIES. MOREOVER, DUE TO THE AVAILABILITY OF A KEY INTERMEDIATE (FIGURE 1B), THE STRAIGHT-FORWARD INCORPORATION OF PHENYL TFVE MOIETIES INTO

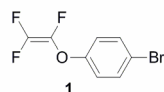
OF CHROMOPHORE SKELETONS SINCE THE LAST DECADE, TFVE-CONTAINING CHROMOPHORE TH  
 HAVE BEEN EXPLORED AS THERMALLY-STABLE NONLINEAR OPTICAL POLYMERS  
 ELECTROLUMINESCENT POLYMERS.

THUS FAR, THE THERMAL, RADICAL INITIATOR-FREE FABRICATION OF SHAPE-PERSISTENT NA  
 DEMONSTRATED. WE ANTICIPATED THAT THE THERMAL REACTIVITY OF TFVES WOULD A  
 NANOPARTICLES. HEREIN WE DESCRIBE THE SYNTHESIS OF RYLENE DYES FUNCTIONALIZED W  
 TFVE MOIETIES AND THE FABRICATION OF RYLENE NANOPARTICLES VIA A THERMAL EMULSION

(A)



(B)



**Figure 1.** (A) THERMAL DIMERIZATION REACTION OF ARYL TRIFLUOROVINYL ETHERS (TFVES),  
 TFVE. (B) STRUCTURE OF 4-BROMOPHENYL TFVE (1).

## Materials and Methods

*General Considerations:* SYNTHETIC MANIPULATIONS WERE CARRIED OUT UNDER ARGON USING I  
 STANDARD SCHLENK TECHNIQUES. ALL SOLVENTS WERE OF ACS REAGENT GRADE OR BETTER  
 1,4-DIOXANE AND 1,2-DIMETHOXYETHANE WERE PURIFIED BY DISTILLATION OVER ACTIVATED  
 (40-63  $\mu$ M) WAS OBTAINED FROM SILICYCLOTRICHLORIDE, AND S-PHOS WERE PURCHASED FROM STR  
 CHEMICALS AND USED WITHOUT FURTHER PURIFICATION. TETRAGLYME WAS PURCHASED FRO  
 PASSING THROUGH A PLUG OF ACTIVATED NEUTRAL ALUMINA. <sup>15</sup>N, <sup>13</sup>C, <sup>16</sup>O, <sup>17</sup>C COMPOUNDS WERE  
 SYNTHESIZED FOLLOWING PUBLISHED PROCEDURES. ULTRAVIOLET-VISIBLE ABSORPTION SPEC

AN AGILENT 8453 DIODE ARRAY SPECTROPHOTOMETER AND CORRECTED FOR BACKGROUND FILLED CUVETTE. FLUORESCENCE SPECTRA WERE MEASURED ON A FLUORESCENCE SPECTROMETER (MODEL FL-321, 450 W XENON LAMP) USING RIGHT-ANGLE DETECTION. FLUORESCENCE LIFETIMES WERE MEASURED USING FREQUENCY MODULATION USING A HORIBA-JOBIN-YVON MF2 LIFETIME SPECTROMETER EQUIPPED WITH A LASER DIODE AND USING THE MODULATION OF POPOP AS A CALIBRATION REFERENCE. MIXTURES OF BIPHASIC MIXTURES WERE EMULSIFIED WITH EITHER AN IKA ULTRA-TURRAX T25 BASIC HIGH-SPEED MIXER (SHEAR RATE OF 24/MIN) OR A MISONIX MICROSON ULTRASONIC CELL DISRUPTOR. DLS MEASUREMENTS WERE PERFORMED AT THE MIT BIOPHYSICS INSTRUMENTATION FACILITY USING A WYATT TECHNOLOGY DLS SYSTEM. DYNAMIC LIGHT SCATTERER EQUIPPED WITH A 830 NM DIODE LASER. DATA WERE FITTED TO A BIEXPONENTIAL MODEL, TAKING INTO ACCOUNT SOLVENT REFRACTIVE INDICES AND VISCOSITIES (WATER: 0.01 CP AT 20°C, TETRAGLYME: 4.1 CP AT 20°C, WATER: 1.00 CP AT 20°C).

*General Procedure for the synthesis of **M1**, **M2**, and **M4**:* A FLAME-DRIED 50 ML SCHLENK FLASK WAS CHARGED WITH THE APPROPRIATE RYBLENEDROMINE SUBSTITUTED (BNA)PCl<sub>3</sub> (0.05 EQ), S-PHOS (0.2 EQ), AND ANHYDROUS POSTASSIUM PHOSPHATE (20 EQ.) UNDER A POSITIVE FLOW OF DEGASSED 1,2-DIMETHOXYETHANE (15ML) WAS INTRODUCED VIA CANNULA ADDITION AND THE REACTION WAS HEATED AT 60°C FOR TWELVE HOURS. THE REACTION WAS COOLED TO ROOM TEMPERATURE AND THE REACTION Mixture WAS FILTERED THROUGH A CELITE PLUG AND THE SOLVENT EVAPORATED UNDER REDUCED PRESSURE. THE RESULTING RESIDUE WAS PURIFIED BY FLASH COLUMN CHROMATOGRAPHY USING 50/50 HEXANES/DICHLOROMETHANE AS THE ELUENT.

**M1**. ISOLATED IN 70% AS A DEEP RED SOLID FROM THE PROCEDURE DESCRIBED ABOVE, WITH SUBSTITUTION OF 3.0M AQUEOUS POTASSIUM PHOSPHATE FOR ANHYDROUS POSTASSIUM PHOSPHATE. <sup>1</sup>H NMR (400 MHZ, CDCl<sub>3</sub>, δ): 8.56 (S, 2H), 8.18 (D, *J* = 8.4 HZ, 2H), 7.80 (D, *J* = 8.4 HZ, 2H), 7.56 (D, *J* = 8.0 HZ, 4H), 7.23 (D, *J* = 8.0 HZ, 4H), 4.11 (M, 4H), 1.92 (M, 2H), 1.55 (S, 6H), 1.32 (M, 20H), 0.91 (M, 14H); <sup>13</sup>C NMR (100 MHZ, CDCl<sub>3</sub>, δ): 163.8, 139.9, 139.4, 136.8, 136.1, 135.0, 131.1, 130.3, 130.1, 129.8, 128.6, 122.5, 121.4, 117.8, 44.5, 38.1, 30.9, 28.9, 24.2, 23.2, 14.3, 10.8; <sup>19</sup>F NMR (376 MHZ, CDCl<sub>3</sub>, δ) -119.00 (DD, *J* = 98, 60 HZ, 1F), -126.69 (DD, *J* = 109, 98 HZ, 1F), -134.47 (DD, *J* = 109, 60



1 HZ, 1F); UV-VIS ( $\text{CHCl}_3$ ):  $\lambda_{\text{MAX}}$ (LOG) = 400 (3.8), 475(3.2), 519 (4.0), 553 (4.4); HRMS (ESI, M/Z):  $[\text{M} + \text{H}]^+$  CALCD FOR  $\text{C}_{10}\text{H}_6\text{F}_6\text{N}_2\text{O}_6$ , 959.3495; FOUND, 959.3493.

2  
3  
4  
5 **M2**. ISOLATED IN 50% AS A DEEP RED SOLID FOLLOWING THE PROCEDURE DESCRIBED ABOVE.  
6  
7 (400 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ): 8.29 (S, 4H), 7.56 (D,  $J = 8.0$  HZ, 8H), 7.23 (D,  $J = 8.0$  HZ, 8H), 4.11 (M, 4H),  
8  
9 1.92 (M, 2H), 1.55 (S, 6H), 1.32 (M, 20H), 0.91 (M, 14H);  $^{13}\text{C}$  NMR (100 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ): 163.7, 139.8,  
10  
11 139.4, 136.8, 135.8, 135.0, 131.1, 130.3, 130.1, 128.6, 122.5, 121.4, 117.8, 44.5, 38.1, 30.9, 28.9, 24.2,  
12  
13 23.2, 14.3, 10.8;  $^{19}\text{F}$  NMR (376 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ) -119.00 (DD,  $J = 98$ , 60 HZ, 1F), -126.69 (DD,  $J = 109$ ,  
14  
15 98 HZ, 1F), -134.47 (DD,  $J = 109$ , 60 HZ, 1F); UV-VIS ( $\text{CHCl}_3$ ):  $\lambda_{\text{MAX}}$ (LOG) = 400 (3.8), 558 (4.0), 592  
16  
17 (4.3); HRMS (ESI, M/Z):  $[\text{M} + \text{H}]^+$  CALCD FOR  $\text{C}_{10}\text{H}_6\text{F}_{12}\text{N}_2\text{O}_8$ , 1303.3767; FOUND, 1303.3769.

18  
19  
20  
21 **M4**. ISOLATED IN 74% AS A GREENISH-BLUE SOLID FOLLOWING THE PROCEDURE DESCRIBED ABOVE.  
22  
23  
24  $^1\text{H}$  NMR (400 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ): 8.37 (S, 4H), 7.98 (S, 4H), 7.56 (D,  $J = 8.4$  HZ, 8H), 7.27 (T,  $J = 4.8$  HZ,  
25  
26 2H), 7.23 (D,  $J = 8.4$  HZ, 8H), 7.01 (D,  $J = 4.8$  HZ, 4H), 2.68 (M, 4H), 1.08 (S, 24H);  $^{13}\text{C}$  NMR (100  
27  
28 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ): 163.3, 155.0, 153.2, 147.8, 145.8, 134.6, 132.1, 132.0, 129.7, 129.2, 129.2,  
29  
30 129.0, 128.9, 128.4, 127.4, 127.3, 126.1, 125.8, 125.5, 124.1, 123.4, 122.7, 122.0, 119.3, 34.7, 29.2,  
31  
32 21.6;  $^{19}\text{F}$  NMR (376 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ) -119.00 (DD,  $J = 98$ , 60 HZ, 1F), -126.69 (DD,  $J = 109$ , 98 HZ, 1F),  
33  
34 -134.47 (DD,  $J = 109$ , 60 HZ, 1F); UV-VIS ( $\text{CHCl}_3$ ):  $\lambda_{\text{MAX}}$ (LOG) = 410 (3.0), 610 (3.1), 665 (3.7), 720  
35  
36 (3.9); HRMS (ESI, M/Z):  $[\text{M} + \text{H}]^+$  CALCD FOR  $\text{C}_{10}\text{H}_6\text{F}_{12}\text{N}_2\text{O}_8$ , 1523.4080; FOUND, 1523.1520.

37  
38  
39  
40 *General Procedure for the synthesis of M3 and M5*: A FLAME-DRIED 50 ML SCHLENK FLASK WAS CHARGED  
41  
42 WITH THE APPROPRIATE RYLENE (BROMIDE OR BROMINE SUBSTITUENT), AND ANHYDROUS POTASSIUM  
43  
44 CARBONATE (1.1 EQ. PER BROMINE SUBSTITUENT) UNDER A POSITIVE FLOW OF NITROGEN. DRY, DMSO  
45  
46 PYRROLIDONE (10ML) WAS INTRODUCED VIA CANNULA ADDITION AND THE RESULTING MIXTURE WAS STIRRED FOR  
47  
48 TWELVE HOURS. THE REACTION WAS COOLED TO ROOM TEMPERATURE, DILUTED WITH 1 M HCl, AND EXTRACTED WITH  
49  
50  $\text{CHCl}_3$  (3X 30 ML). THE ORGANIC LAYERS WERE COMBINED, DRIED OVER MAGNESIUM SULFATE, AND  
51  
52 EVAPORATED UNDER REDUCED PRESSURE. THE RESULTING RESIDUE WAS PURIFIED BY FLASH CHROMATOGRAPHY  
53  
54 USING 60/40 HEXANES/DICHLOROMETHANE AS THE ELUENT.



**M3.** ISOLATED IN 85% AS A DEEP RED SOLID FROM THE PROCEDURE DESCRIBED ABOVE. (400 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ): 9.47 (D,  $J = 8.4$  HZ, 2H), 8.57 (D,  $J = 8.4$  HZ, 2H), 8.23 (S, 1H), 7.18 (M, 8H), 4.04 (M, 4H), 1.87 (M, 2H), 1.57 (S, 4H), 1.28 (M, 22H), 0.88 (M, 16H);  $^{13}\text{C}$  NMR (100 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ): 163.7, 155.3, 139.4, 132.1, 130.5, 129.3, 129.0, 125.3, 124.1, 123.9, 122.4, 121.3, 118.3, 44.5, 38.1, 30.9, 28.9, 24.2, 23.2, 14.3, 10.8 ;  $^{19}\text{F}$  NMR (376 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ) -119.00 (DD,  $J = 98$ , 60 HZ, 1F), -126.69 (DD,  $J = 109$ , 98 HZ, 1F), -134.47 (DD,  $J = 109$ , 60 HZ, 1F); UV-VIS ( $\text{CHCl}_3$ )  $\lambda_{\text{MAX}}$  (LOG) = 400 (3.8), 461 (3.8), 502 (4.1), 536 (4.4); HRMS (ESI, M/Z):  $[\text{M} + \text{H}]^+$  CALCD FOR  $\text{H}_{96}\text{F}_6\text{N}_2\text{O}_8$ , 991.3393; FOUND, 991.3398.

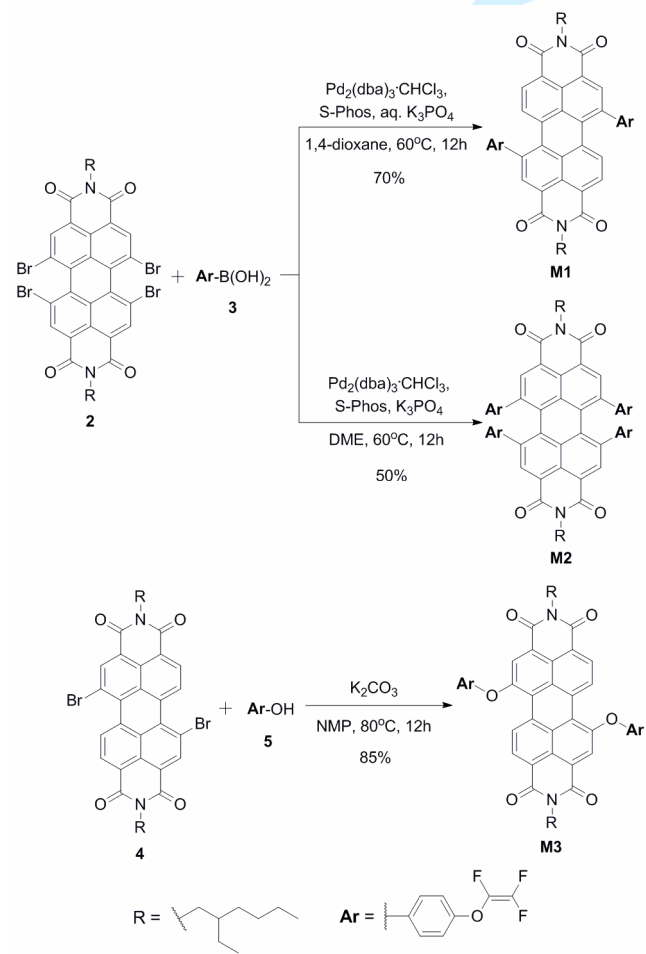
**M5.** ISOLATED IN 87% AS A DEEP BLUE SOLID FROM THE PROCEDURE DESCRIBED ABOVE. (400 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ): 9.47 (S, 4H), 8.27 (S, 4H), 7.40 (D,  $J = 8.4$  HZ, 8H), 7.27 (T,  $J = 4.8$  HZ, 2H), 7.09 (D,  $J = 8.4$  HZ, 8H), 7.01 (D,  $J = 4.8$  HZ, 4H), 2.68 (M, 4H), 1.08 (S, 24H);  $^{13}\text{C}$  NMR (100 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ): 163.3, 155.0, 153.2, 147.8, 145.8, 134.6, 132.1, 132.0, 129.7, 129.2, 129.2, 129.0, 128.9, 128.4, 127.4, 127.3, 126.1, 125.8, 125.5, 124.1, 123.4, 122.7, 122.0, 119.3, 34.7, 29.2, 21.6;  $^{19}\text{F}$  NMR (376 MHZ,  $\text{CDCl}_3$ ,  $\delta$ ) -119.00 (DD,  $J = 98$ , 60 HZ, 1F), -126.69 (DD,  $J = 109$ , 98 HZ, 1F), -134.47 (DD,  $J = 109$ , 60 HZ, 1F); UV-VIS ( $\text{CHCl}_3$ )  $\lambda_{\text{MAX}}$  (LOG) = 410 (3.2), 569 (3.8), 623 (4.0), 680 (4.2); HRMS (ESI, M/Z):  $[\text{M} + \text{H}]^+$  CALCD FOR  $\text{H}_{96}\text{F}_{12}\text{N}_2\text{O}_{12}$ , 1587.3876; FOUND, 1587.3877.

*Nanoparticle Synthesis.* 0.5 ML OF A SOLUTION OF THE APPROPRIATE TFVE-FUNCTIONALIZED RY MONOMER IN MESITYLENE (0.2 – 1.6 MG/ML) WAS ADDED TO 5.0 ML TETRAGLYME. THE RESULTING MIXTURE WAS EITHER HOMOGENIZED WITH A HIGH-SHEAR DISPERSER OR SONICATED TO FORM AN EMULSION, WHICH WAS THEN HEATED FOR 90 MIN FOR 12 H.

## Results and Discussion

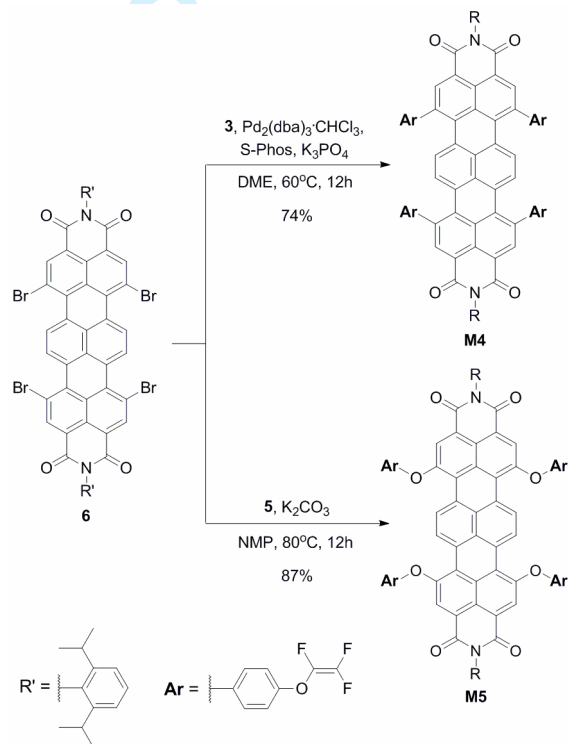
**Monomer Synthesis.** PDIS WERE BAY-FUNCTIONALIZED WITH PHENYL TFVE MOIETIES STARTING FROM TETRABROMIDE OR DIBROMIDE (SCHEME 1). FOLLOWING THE PREVIOUSLY REPORTED SYNTHESIS

CSF/AGO MEDIATED TETRAARYLAZATION OF **2** INITIALLY AIMED TO PERFORM A FOUR-FOLD SUZUKI COUPLING BETWEEN **2** AND **3**. HOWEVER, THE TFVE MOIETY WAS FOUND TO BE SLIGHTLY SUSCEPTIBLE TO NUCLEOPHILIC ADDITION OF FLUORIDE IN THE PRESENCE OF A BASE SYSTEM AND THE RESULTING HYDROLYTICALLY DEGRADED 1,2,2-FLUOROETHANE-CONTAINING (3,5)-DIFLUOROPHENYL-CONTAINING PRODUCTS COULD NOT BE SEPARATED FROM THE MIXTURE. INSTEAD, A FOUR-FOLD SUZUKI-MIYaura CROSS COUPLING UNDER THE MODIFIED CONDITIONS WAS PURSUED. WHEN AQUEOUS POTASSIUM PHOSPHATE WAS EMPLOYED AS A BASE, TETRAARYLBROMIDE **2** AND MONOMER **3** REACTED TO GIVE **M1**, A PERYLENE DIIMIDE-CONTAINING MONOMER TWO PHENYL TFVE MOIETIES, WAS ISOLATED IN 70% YIELD. SWITCHING THE BASE TO RIGOROUSLY ANHYDROUS POTASSIUM PHOSPHATE, **M2** WAS TETRAARYLAZED TO GIVE **M2**, WHICH WAS ISOLATED IN 50% YIELD. TAKING ADVANTAGE OF THE ELECTRON-DEFICIENT NATURE OF THE PERYLENE DIIMIDE, **M3** WAS SYNTHESIZED VIA A REACTION BETWEEN **4** AND **5**.



**Scheme 1.** SYNTHESIS OF PERYLENE DIIMIDE-CONTAINING THERMOSET MONOMERS.

THE SYNTHESIS OF TFVE-FUNCTIONALIZED TERRYLENE DIIMIDE (TDI) MONOMERS IS SHOWN IN SCHEME 2. SIMILAR TO MONOMER **M2**, THE TETRAARYLATED TDI MONOMER **M4** WAS SYNTHESIZED STARTING FROM TETRA-BROMIDOTERRYLENE DIIMIDE **6** BY A MODIFIED SUZUKI-MIYaura CROSS-COUPLING REACTION WITH ANHYDROUS POTASSIUM PHOSPHATE. MONOMER **M5** WAS SYNTHESIZED BY A REACTION BETWEEN **6** AND **5**.



**Scheme 2.** SYNTHESIS OF TERRYLENE DIIMIDE-CONTAINING THERMOSET MONOMERS.

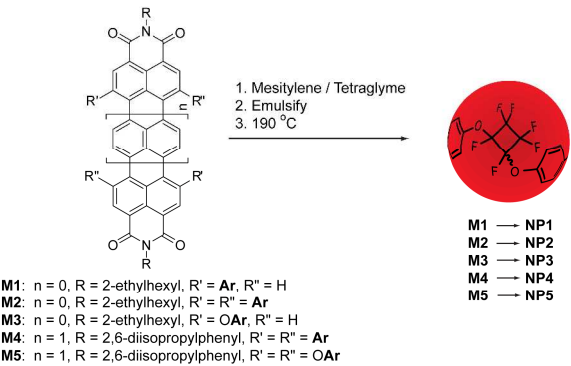
**Monomer Photophysics.** THE PHOTOPHYSICAL PROPERTIES OF MONOMERS (SOLUTIONS) ARE SUMMARIZED IN TABLE 1. IN GENERAL, THE TFVE MOIETIES WERE NOT OBSERVED TO SIGNIFICANTLY AFFECT THE OPTICAL PROPERTIES OF RYLENE DYES. THE ABSORPTION AND EMISSION MAXIMA AND FLUORESCENCE QUANTUM YIELDS OF MONOMERS **M3** AND **M5** WERE SIMILAR TO PHENYLOXY-SUBSTITUTED PDI, RESPECTIVELY. MONOMER **M2** DISPLAYED SIMILAR ABSORPTION AND EMISSION MAXIMA TO THE PREVIOUSLY-REPORTED PDI. CONSISTENT WITH SIMILAR OBSERVATIONS FOR BIPHENYL-CONTAINING SUBSTITUTIONS, THE PRESENCE OF TFVE MOIETIES WAS FOUND TO INCREASE THE OTHERWISE-SMALL STOKES' SHIFT OF RYLENE DYES AND DECREASE THE FLUORESCENCE QUANTUM YIELDS. MOREOVER, THE EXCITED-STATE LIFETIMES OF THE PHENYLOXY-SUBSTITUTED PDI, **M2** AND **M5** WERE

M4, WERE FOUND TO BE SIGNIFICANTLY LONGER THAN THEIR PARENT RY(2-ETHYLHEXYL)4.5 NS FOR PDI AND 3.5 NS FOR 2,6-DIISOPROPYLPHENYL)-TDI), MOST LIKELY DUE TO EXCITED STATE PLANA THE BIPHENYL LINKAGE.

Table 1. PHOTOPHYSICAL PROPERTIES) OF PHENYL TFVE-CONTAINING RYLENE DIIMIDES.

COMPOUND	$\lambda_{\text{MAX}} / \text{NM}$ (LOG)	$\lambda_{\text{EM}} / \text{NM}$	$\Phi$	$\tau / \text{NS}$
M1	553 (4.4)	602	0.88 <sup>A</sup>	8.7
M2	592 (4.3)	640	0.61 <sup>A</sup>	9.8
M3	536 (4.4)	563	0.81 <sup>A</sup>	5.8
M4	720 (3.9)	765	0.08 <sup>B</sup>	5.7
M5	680 (4.2)	700	0.17 <sup>B</sup>	2.4

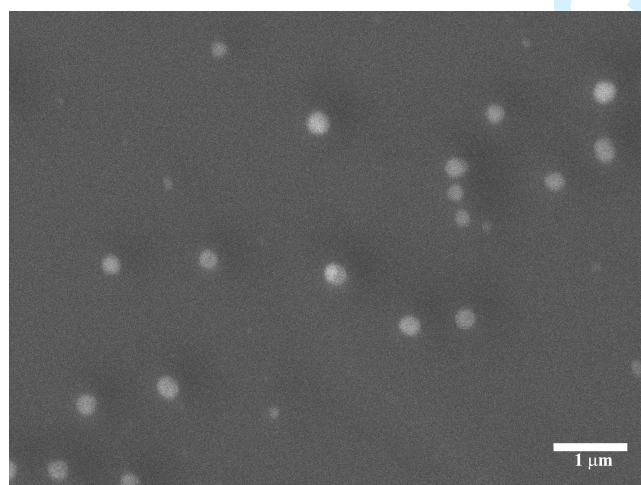
<sup>A</sup> MEASURED AGAINST RHODAMINE B IN ETHANOL, <sup>B</sup> MEASURED AGAINST ZINC PHTHALOCYANINE I PYRIDINE IN TOLUENE)



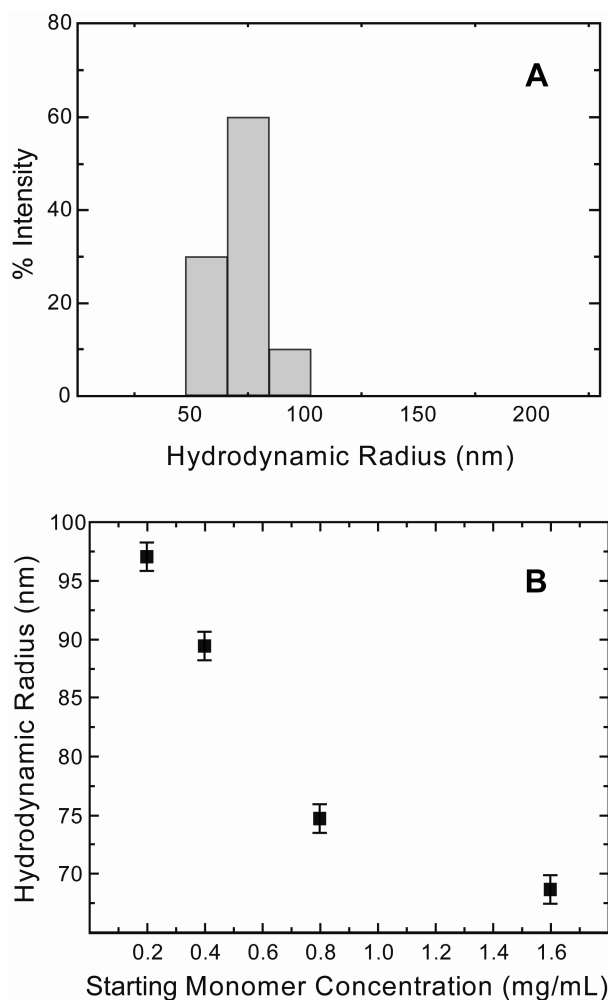
Scheme 3. THERMAL FORMATION OF SHAPE-PERSISTENT RYLENE NANOPARTICLES.

Nanoparticle Synthesis. RYLENE NANOPARTICLES WERE SYNTHESIZED BY ADDING MESITYLENE MONOMERS 1-5 TO TETRAGLYME AND EITHER HOMOGENIZING OR SONICATING THE RESULTING

THIS HOMOGENEOUS MIXTURE WAS THEN THERMALLY CROSSLINKED FOR TWENTY-FOUR HOURS (SCHEME 3). SCANNING ELECTRON MICROGRAPH (SEM) IMAGES OF THE DROP-CAST REACTION MIXTURE OBTAINED FROM REVEALED THE PRESENCE OF POLYDISPERSE, SUBMICRON PARTICLES (SEE FIGURE 3A). LIGHT SCATTERING (DLS) MEASUREMENTS ON THE THERMALLY-POLYMERIZED MIXTURES FOR TETRAGLYME INDICATED THAT PARTICLES WITH HYDRODYNAMIC RADII BETWEEN CA. 70 AND 100 NM IN TETRAGLYME (SEE FIGURE 3A). A SIGNIFICANT DIFFERENCE WAS NOT OBSERVED IN THE SIZE OF THE NANOPARTICLES OF PERYLENE NP(1-3) VERSUS TERRYNE NP(4-5) (DIIMIDE MONOMERS). THE SIZE OF THE DYE PARTICLES IN TETRAGLYME COULD BE CONTROLLED WITHIN THE 70 – 100 NM RANGE BY VARYING THE CONCENTRATION OF THE DYE IN THE STARTING MESITYLENE SOLUTION (SEE FIGURE 3B). DLS MEASUREMENTS DID NOT INDICATE COAGULATE IN TETRAGLYME FOR AT LEAST SIX MONTHS (THE STABILITY OF THE NANOPARTICLES IN TETRAGLYME WAS ONLY MONITORED FOR SIX MONTHS).



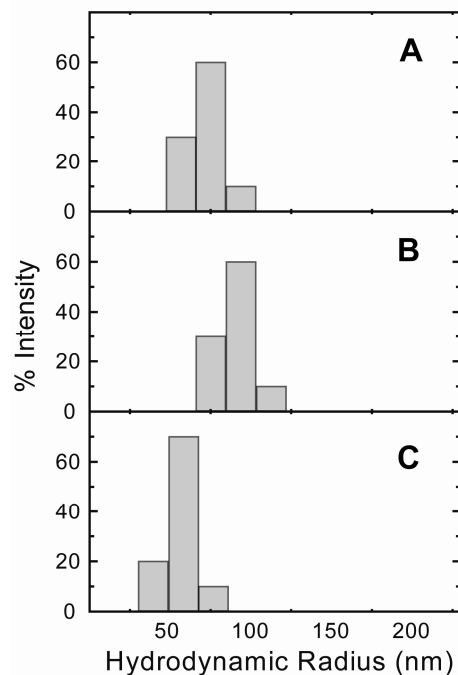
**Figure 2.** SEM MICROGRAPH OF THE THERMALLY-POLYMERIZED REACTION MIXTURE OBTAINED FROM



**Figure 3.** (A) TYPICAL DISTRIBUTION OF HYDRODYNAMIC RADII IN TETRAGLYME FOR THE THE MIXTURES FABRICATED WITH AS MEASURED BY DYNAMIC LIGHT SCATTERING (DLS); THE PAIR DISTRIBUTION FUNCTIONS SHOWN (1.6 MG/ML STARTING MONOMER CONCENTRATION IN MESITYLENE) (B) AVERAGE HYDRODYNAMIC RADII OF PARTICLES OBTAINED BY VARYING THE CONCENTRATION OF STARTING MESITYLENE SOLUTION (SHOWN FOR NP2)

ONCE THERMALLY POLYMERIZED, THE CHROMOPHORE NANOPARTICLES COULD BE EXTRACTED FROM THE TETRAGLYME SUSPENSIONS. SPECTRA OF *the* *ene-d<sub>8</sub>* extract OF THE THERMALLY-POLYMERIZED REACTION MIXTURE OBTAINED FROM THAT THE DESIRED FORMATION OF PFC PROCEEDED, AS THE THREE CHARACTERISTIC DOUBLET OF DOUBLETS ARISING FROM THE T OBSERVED (SEE SUPPORTING INFORMATION). ADDITIONALLY, UNDESIRE SIDE PRODUCTS FROM OR OTHER NUCLEOPHILES TO THE TFVE MOIETY WERE NOT DETECTED IN THE NANOPARTICLES

NP2, NP4 AND NP5 WERE OBSERVED TO RETAIN THEIR SHAPE UPON EXTRACTION INTO ORGANIC  
AND CHCl<sub>3</sub>. HOWEVER, THE HYDRODYNAMIC RADII OF THESE PARTICLES WERE OBSERVED  
APPROXIMATELY 30% IN ORGANIC SOLVENTS (SEE FIGURE 4).

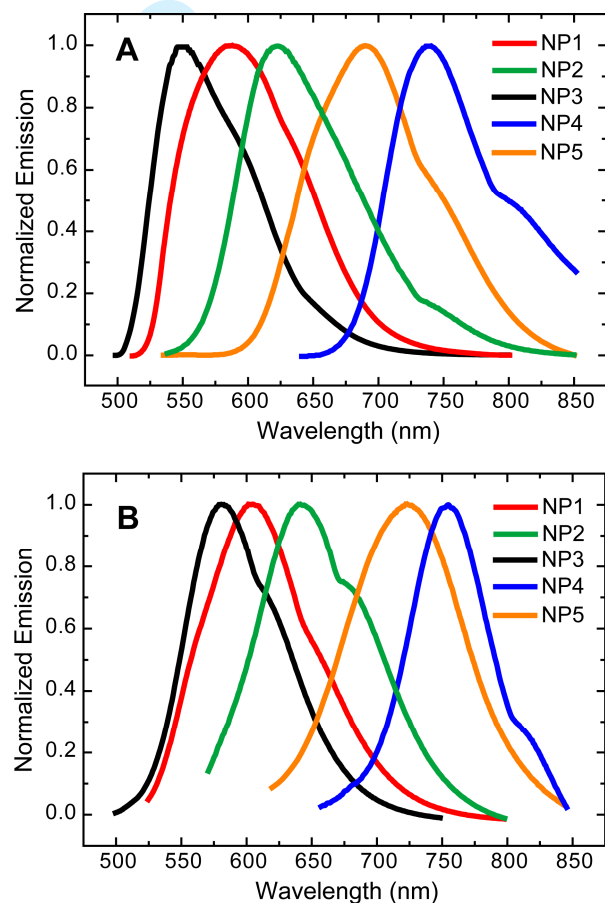


**Figure 4.** TYPICAL CHANGES IN THE MEASURED HYDRODYNAMIC RADII FOR NP2, NP4 AND NP5 WITH CHANGING SOLVENTS. THE PARTICLE SIZE DISTRIBUTION FOR NP2 (CONCENTRATION OF 1.6 MG/ML STARTING MONOMER CONCENTRATION IN MESITYLENE) IS SHOWN IN (A) TETRAGLYME, (B) TOLUENE AND (C) WATER.

**Nanoparticle Photophysics.** THE ABSORPTION AND EMISSION SPECTRA OF NP2 IN TETRAGLYME (FIGURE 5A) WERE, OVERALL, SIMILAR TO THOSE OF THEIR RESPECTIVE MONOMERS IN CHCl<sub>3</sub> SOLUTIONS, WITH TWO NOTABLE DIFFERENCES: THE ABSORPTION AND EMISSION BANDS OF THE MONOMERS WERE BROADENED AND THEIR EMISSION MAXIMA WERE HYPSOCHROMICALLY SHIFTED BY APPROXIMATELY 10-20 nm RELATIVE TO THEIR CORRESPONDING MONOMERS. WE TENTATIVELY ASCRIBE THESE OBSERVATIONS TO THE RYLENE CHROMOPHORES IN THE PRESENCE OF TETRAGLYME. ACCORDINGLY, THE FLUORESCENCE



THE NANOPARTICLES IN TETRAGLYME WERE ALSO SLIGHTLY LOWER THAN THOSE OF THE STABLE NANOPARTICLES. A LOSS IN FLUORESCENCE QUANTUM YIELD WAS GENERALLY OBSERVED AFTER THERMAL EMULSION POLYMERIZATION IN TETRAGLYME.



**Figure 5.** EMISSION SPECTRA OF NP1-NP5 AS COLLOIDAL SUSPENSIONS IN TETRAGLYME (A) AND AQUEOUS SUSPENSIONS IN WATER (B, 1:50 DILUTION OF THE TETRAGLYME SUSPENSION INTO DI WATER).

THE NANOPARTICLE SUSPENSIONS IN TETRAGLYME WERE DILUTED INTO WATER (1:50 DILUTION). THE AQUEOUS MIXTURES WERE FILTERED THROUGH A FILTER TO REMOVE LARGE AGGREGATES. THE AQUEOUS SOLUTIONS WERE HOMOGENOUS AND NANOPARTICLE PRECIPITATION WAS NOT OBSERVED. MEASUREMENTS REVEALED THAT THE HYDROPHOBICITY INCREASED BY CA. 35% RELATIVE TO THOSE MEASURED IN TETRAGLYME (SEE FIGURE 4). THESE AQUEOUS SOLUTIONS REMAINED HOMOGENOUS.

THE MEASURED HYDRODYNAMIC RADII OF THE NANOPARTICLES REMAINED UNCHANGED FOR  
THE EMISSION SPECTRA IN CHN WATER ARE SHOWN IN FIGURE 5B. THE EMISSION MAXIMA OF  
WATER ARE VERY SIMILAR TO THOSE OF THEIR CORRESPONDING MONOMERS IN CHLOROFO  
SOLUTIONS OF THE PERYLENE DIIMIDE NANOPARTICLES<sup>3</sup> DISPLAYED GOOD FLUORESCENCE  
QUANTUM YIELDS (63%, 50% AND 60%, RESPECTIVELY); HOWEVER, THE FLUORESCENCE QU  
AQUEOUS SOLUTIONS OF THE TERRYLENE DIIMIDE NANOPARTICLES<sup>3</sup> WERE RELATIVELY LOW (3% AND  
11%, RESPECTIVELY).

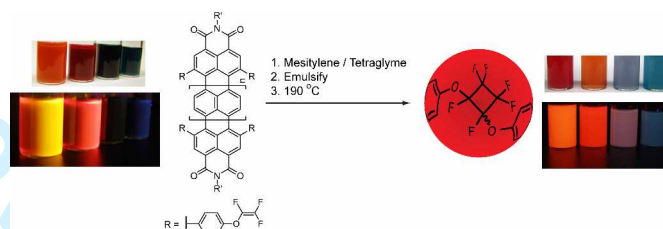
## Conclusions

RYLENE DYES FUNCTIONALIZED WITH VARYING NUMBERS OF PHENYL TRIFLUOROVINYLETH  
SYNTHESIZED AND SUBJECTED TO A THERMAL EMULSION POLYMERIZATION TO YIELD SHAPE-P  
CHROMOPHORE NANOPARTICLES. THE REPORTED THERMAL EMULSION POLYMERIZATION IS U  
REPORTED METHODS TO FABRICATE CHROMOPHORE OR CONJUGATED POLYMER NANOPARTIC  
THE USE OF RADICAL INITIATORS OR METAL CATALYSTS. AQUEOUS SOLUTIONS OF PERYL  
NANOPARTICLES REMAINED HOMOGENOUS FOR AT LEAST THREE MONTHS AND DISPLAYED  
QUANTUM YIELDS.

**Supporting Information Available.** <sup>19</sup>F NMR SPECTRA OF SELECT SYSTEMS AND SPECTRAL CHARA  
DATA.

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FELLOWSHIP. THE BIOPHYSICAL INSTRUMENTATION FACILITY FOR THE STUDY OF COMPL  
SYSTEMS (NSF-0070319 AND NIH GM68762) IS GRATEFULLY ACKNOWLEDGED.

## TOC graphic.



RYLENE DYES FUNCTIONALIZED WITH VARYING NUMBERS OF PHENYL TRIFLUOROVINYLETHYL GROUPS WERE SYNTHESIZED AND SUBJECTED TO A THERMAL EMULSION POLYMERIZATION TO YIELD SHAPE-PERSISTENT CHROMOPHORE NANOPARTICLES. SUSPENSIONS OF THE RYLENE NANOPARTICLES IN WATER SHOWED HIGH QUANTUM YIELDS.

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**Selective Detection of Explosives via Photolytic Cleavage of Nitroesters and Nitramines**

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# SELECTIVE DETECTION OF EXPLOSIVES VIA PHOTOFRAGMENTATION AND CLEAVAGE OF NITROESTERS AND NITRAMINE

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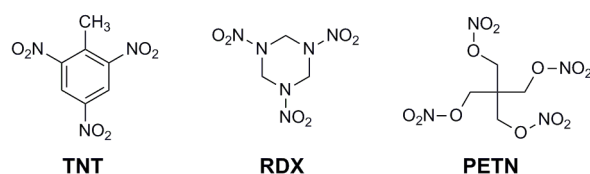
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**ABSTRACT.** THE NITRAMINE-CONTAINING EXPLOSIVE RDX AND THE NITROESTER-CONTAINING PETN ARE SHOWN TO BE SUSCEPTIBLE TO PHOTOFRAGMENTATION UPON EXPOSURE TO SUNLIGHT. NITROESTER- AND NITRAMINE-CONTAINING MOIETIES ARE ALSO SHOWN TO FRAGMENT UPON IRRADIATION. THE PRODUCTS OF THIS PHOTOFRAGMENTATION ARE REACTIVE, ELECTROPHILIC NITROUS AND NITRIC ACID, NITRIC OXIDE, AND NITROGEN DIOXIDE. 9,9-DISUBSTITUTED 9,10-DIHYDROACRIDINES (DHAS) ARE SYNTHESIZED FROM NITRIC ACID METHYL ESTER OR A DIPHENYLAMINE DERIVATIVE AND ARE SIMILARLY SHOWN TO BE RA- PHOTOFRAGMENTATION PRODUCTS OF RDX AND PETN. A NEW (TURN-ON) EMISSION SIGNAL AT 365 nm UPON NITRATION OF DHAS DUE TO THE GENERATION OF FLUORESCENT DONOR-ACCEPTOR COMPLEXES. BY FLUORESCENCE SPECTROSCOPY, THE PRESENCE OF CA. 1.2 NG OF RDX AND 320 PG OF PETN CAN BE DETECTED. DHAS INDICATORS IN THE SOLID STATE UPON EXPOSURE TO SUNLIGHT. THE NITRATION OF AR- PHOTOFRAGMENTATION PRODUCTS OF RDX AND PETN IS PRESENTED AS A UNIQUE, HIGHLY SENSITIVE MECHANISM FOR NITROESTER- AND NITRAMINE-CONTAINING EXPLOSIVES AND DHAS ARE PRE-

AND IMPERMANENT FLUOROGENIC INDICATORS FOR THE SELECTIVE, STANDOFF/REMOTE IDENTIFICATION OF PETN.

## Introduction

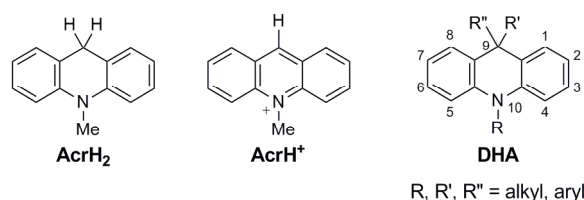
DETECTING HIDDEN EXPLOSIVE DEVICES IN WAR ZONES AND TRANSPORTATION HUBS IS AN IMPORTANT TASK. THREE MOST COMMONLY USED HIGHLY ENERGETIC COMPOUNDS IN EXPLOSIVE FORMULATIONS ARE TRINITROTOLUENE (TNT), 1,3,5-TRINITROTRIAZINANE (RDX), AND PENTAERYTHRITOL TETRANITRATE (PETN). NUMEROUS TECHNOLOGIES ARE CURRENTLY CAPABLE OF DETECTING THE ENERGETIC CHEMICALS IN HIDDEN EXPLOSIVE DEVICES, INCLUDING: ANALYTICAL SPECTROMETERS USING EITHER SMALL-SCALE FLUOROPHORS OR FLUORESCENT CONJUGATED CHEMISISTIVE SENSORS, PORTABLE MASS SPECTROMETERS, AND X-RAY SYSTEMS. EACH EXAMPLE LISTED HAS UNIQUE ADVANTAGES AND LIMITATIONS. FOR INSTANCE, WHILE X-RAY SYSTEMS ARE CAPABLE OF DETECTING BULK HIDDEN EXPLOSIVE DEVICES, MASS SPECTROMETERS ARE CAPABLE OF IDENTIFYING THE EXACT CHEMICAL STRUCTURES OF SUSPECTED COMPOUNDS. THE DEPLOYMENT AND/OR LONGEVITY OF THESE HARDWARE-INTENSIVE TECHNOLOGIES IN COMPLEX ENVIRONMENTS IS TRIVIAL. FLUORESCENT SENSORS ARE COMPARATIVELY TECHNOLOGY-UNINTENSIVE, HAVE DEPENDABLE LIMITS, AND ARE ALSO CAPABLE OF IDENTIFYING (RESPONDING TO) MOLECULES (SUCH AS NITROAROMATICS) OR PARTICULAR FUNCTIONAL GROUPS (ALDEHYDES). THESE SENSORS CAN BE MORE SPECIFIC THAN FLUORESCENT SENSORS BUT ARE NOT AS SENSITIVE AND DO NOT HAVE THE ANALYTICAL SIGNAL, SUCH AS REMOTE LINE-OF-SIGHT (STAND-OFF) DETECTION OR PROSPECTS FOR COMPLEX DETECTION. FLUORESCENCE LIFETIMES, DEPOLARIZATION).



**Figure 1.** STRUCTURES OF COMMON HIGH EXPLOSIVES.

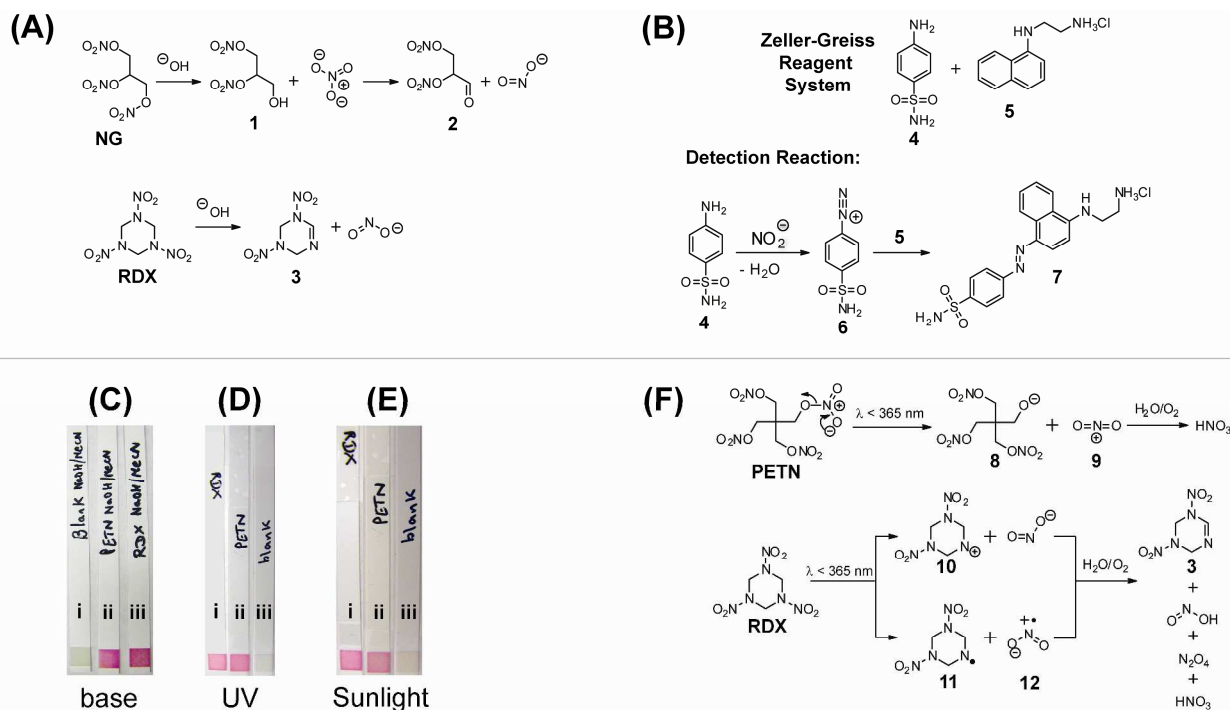
WE PREVIOUSLY REPORTED A TURN-ON FLUORESCENCE CHEMOSENSING SCHEME BASED ON THE INTERACTION BETWEEN A HYDRIDE DONOR AND EITHER RDX OR PETN, WHEREIN THE NITRAMINE OR NITRO

PHOTOREDUCED BY 9,10-DIHYDROACRIDINE (FIGURE 2) OR ITS METALATED ANALOGUES. THE PRODUCT  $\text{AcrH}^+$  OF THIS PHOTOREACTION HAD A HIGH FLUORESCENCE QUANTUM YIELD AND A SIGNIFICANT FLUORESCENCE TURN-ON SIGNAL IN THE PRESENCE OF RDX AND PETN.



**Figure 2.** STRUCTURES OF THE HYDROACRIDINE AND THE 9,9-DISUBSTITUTED 9,10-DIHYDROACRIDINES, DHA, DIHIED HEREIN.

WHILE STUDYING THIS PHOTOREACTION, WE BECAME INTERESTED IN THE PHOTOCHEMICAL AND NITROESTER COMPOUNDS UNDER ULTRAVIOLET (UV) IRRADIATION. NITROESTERS AND KNOWN TO DEGRADE UNDER HIGHLY ACIDIC OR BASIC CONDITIONS AND ESTABLISHED SPOT TO DETECT THESE CHEMICAL DEGRADATION PRODUCTS AS OPPOSED TO DIRECTLY DETECTING IN BASE-PROMOTED DIGESTION OF NITROGLYCERIN (NG) HAS ALSO BEEN STUDIED AND IS THOUGHT OF NITRATE AND NITRITE ANIONS, AMONG OTHER DEGRADATION PRODUCTS, (SOME ALSO KNOWN TO DECOMPOSE IN BASIC MEDIA AND PRODUCE NITRITE IONS). THE GREISS TEST FOR NITRITE IONS CAN, THEREFORE, BE EMPLOYED TO CONFIRM THE EVOLUTION OF NITRITE UPON BASE-PROMOTED DIGESTION OF RDX AND PETN. THE CHEMISTRY BEHIND THE COMMERCIALY-AVAILABLE GREISS TEST (SCHEME 1) INVOLVES THE REACTION OF SULFANILAMIDE WITH NITRITE TO FORM DIAZOTIZED SULFANILAMIDE, WHICH THEN REACTS WITH AN ARYLAMINE (5) TO FORM A BRIGHTLY-COLORED AZO DYE. IN SCHEME 1C, WHEN NITRITE TEST STRIPS IMPREGNATED WITH THE MODIFIED GREISS REAGENT WERE DIPPED INTO SOLUTIONS OF EITHER RDX OR PETN IN 1 M NaOH, A BRIGHT PINK COLOR EVOLVED, INDICATING THE PRESENCE OF NITRITE ANIONS.



**Scheme 1.** (A) DEGRADATION MECHANISMS OF NITROESTERS AND NITRAMINES IN BASIC ME COMPONENTS AND DETECTION MECHANISM OF THE ZELLER-GREISS TEST FOR NITRITE IONS. (B) BASE-DEGRADED RDX AND PETN. TEST STRIPS WERE DIPPED INTO BLANK 2:1 MECN: 1M NAOH (I) PETN (II) OR 10 MG RDX (III) IN 3 ML 2:1 MECN: 1M NAOH. (D) NITRITE ION TEST ON PHOTOLYZED RDX AND PETN. TEST STRIPS WERE DIPPED INTO (I) 10 MG RDX OR (II) 15 MG PETN IN 3 ML MECN, OR (III) 15 MG PETN IN 3 ML MECN AND IRRADIATED AT 254 NM FOR ONE MINUTE. (E) NITRITE ION TEST ON RDX AND PETN IN 3 ML MECN AND IRRADIATED WITH POLYCHROMATIC LIGHT FROM A SOLAR SIMULATOR FOR 30 MIN. (F) PHOTOLYTIC CLEAVAGE PATHWAY OF NITROESTERS AND NITRAMINES AND SELECT PHOTOFRACTIONATION.

INTERESTINGLY, WHEN THE SAME NITRITE TEST STRIPS WERE DIPPED INTO BASE-FREE ACETONE OR PETN, DRIED AND IRRADIATED AT 254 NM, FORMATION OF THE PINK AZO DYE WAS ALSO OBSERVED (Figure 1D), SUGGESTING THE EVOLUTION OF NITRITE IONS UPON THE PHOTOLYSIS OF RDX AND PETN. IRRADIATION AT 254 NM, 334 NM AND 365 NM SIMILARLY RESULTED IN A POSITIVE GREISS TEST; HOWEVER, NON-UV

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YIELD A PINK COLOR. MOREOVER, EXTENDED EXPOSURE (30 MINUTES) TO POLYCHROMATIC  
SIMULATOR WAS ALSO OBSERVED TO PHOTOLYZE RDX AND PETN AND YIELD A POSITIVE GREISS.  
THE PHOTOLYSIS OF NITROESTER AND NITRAMINE-BASED ENERGETIC COMPOUNDS UNDER V  
BEEN STUDIED AND FOUND TO PRODUCE A NUMBER OF SMALL-MOLECULE DEGRADATION PRO  
AND NITRIC ACID, NITRIC OXIDE, NITROGEN DIOXIDE, FORMALDEHYDE, PROPOSED HETEROLYTIC  
DEGRADATION MECHANISMS FOR PETN AND RDX ARE SHOWN IN SCHEME 1F. IN THE CASE O  
HYPOTHESIZED THAT HETEROLYTIC CLEAVAGE OF THE C-NO<sub>2</sub> BOND IN RDX PRODUCES AN ANIONIC  
REACTIVE NITRONIUM ION (12) THAT RAPIDLY FORMS NITRIC ACID UNDER AMBIENT CONDITIONS. EVIDENCE  
OF BOTH THE HOMOLYTIC AND HETEROLYTIC SCISSION OF THE C-NO<sub>2</sub> BOND TO PRODUCE NITROGEN DIOX  
(12) OR NITRITE, RESPECTIVELY) EXISTS AND THE EXACT NATURE OF THE INITIAL PHOTOREACT  
NEVERTHELESS, IT CAN BE AGREED THAT THE PROPOSED INITIAL PRODUCTS OF RDX AND PETN  
REACTIVE, ELECTROPHILIC SPECIES, WHICH CAN CONCEIVABLY CONVERT 4-SULFANYLAMINE  
CATION 6 NECESSARY TO PRODUCE A POSITIVE RESULT IN THE ZELLER-GREISS TEST.

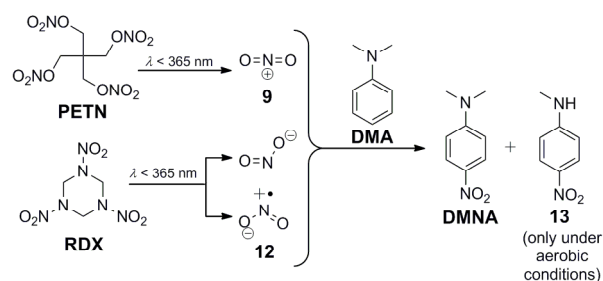
UNFORTUNATELY, THE GREISS TEST OR VARIATIONS THEREOF CANNOT MEET THE DETECTION  
AND PETN. FIRST, SIMPLE STANDOFF DETECTION (DETECTION AT A DISTANCE) WITH COLORIMETRY IS  
VIABLE POSSIBILITY BECAUSE OF THE DIFFICULTY IN GETTING A CLEAR OPTICAL SIGNAL IN  
ABSORPTIVE PROCESS. MOREOVER, EVEN WITH OPTIMIZED REAGENT SYSTEMS, THE DETECTION  
IS IN THE MICROGRAM RANGE, WHICH IS NOT COMPETITIVE WITH EXISTING METHODS TO DETECT RDX

HEREIN, WE PROPOSE INSTEAD A SENSING SCHEME THAT IS UNIQUELY SELECTIVE TO THE PHOTOLYSIS OF  
NITROESTER AND NITRAMINE COMPOUNDS THROUGH THE FORMATION OF NITROAROMATIC PRO  
FLUORESCENCE SIGNAL. THE PRO-FLUORESCENT, OR FLUOROGENIC, INDICATORS DESCRIBED  
EFFICIENTLY REACTING WITH THE PHOTOFRAGMENTS OF RDX AND PETN AND CONSTITUTE A  
AND SENSITIVE DETECTION SCHEME FOR THESE EXPLOSIVES.



## Results and Discussion

**Indicator Design.** CONSIDERING THE ELECTROPHILIC NATURE OF THE SPECIES GENERATED BY THE PHOTOFRAGMENTATION OF RDX AND PETN AND THEIR RESEMBLANCE TO THE ACTIVE ELECTROPHILIC SPECIES INVOLVED IN NITRATION REACTIONS, WE TARGETED REACTIONS BETWEEN ELECTRON-RICH TERTIARY ANILINES AND PHOTOFRAGMENTS OF RDX AND PETN. IT WAS FOUND THAT IRRADIATION OF A MIXTURE OF DIMETHYLANILINE (DMA) AND 2 EQUIVALENTS OF EITHER RDX OR PETN FOR 10 MINUTES IN AN ANAEROBIC CONDITIONS AFFORDED THE FORMATION OF 4-NITROANILINE (DMNA) IN 14% YIELD (CALCULATED FROM DMA). HIGHER YIELDS OF DMNA WERE OBTAINED WITH LONGER PHOTOLYSIS TIMES AND DMA. CA. 80% YIELD AFTER 1 HOUR. THE PHOTOREACTION BETWEEN DMA AND EITHER RDX OR PETN UNDER ANAEROBIC CONDITIONS WAS OBSERVED TO PRODUCE ONLY A YELLOW-COLORED PRODUCT (DMNA) AND OTHER PRODUCTS WERE NOT EVIDENT BY TLC OR GC-MS ANALYSIS. THE HIGH-RESOLUTION MASS SPECTRA OF THE ISOLATED YELLOW PRODUCT EXACTLY MATCHED THOSE OBTAINED FOR A SAMPLE OF DMNA. CONDUCTING THE PHOTOLYSIS UNDER AEROBIC CONDITIONS RESULTED IN THE CONSUMPTION OF DMA<sup>16</sup> AND YIELDED A MIXTURE OF DMNA AND ITS DEMETHYLANILINE (DMNA) (SEE SCHEME 2). PHOTOLYSIS OF DMA WITH AMMONIUM NITRATE WAS ALSO FOUND TO PRODUCE DMNA ALTHOUGH LONGER PHOTOLYSIS TIMES (>30 MINUTES) WERE REQUIRED AND GREATER AMOUNTS OF DMA WERE CONSUMED. UNDER AEROBIC CONDITIONS, ADDITIONAL PRODUCTS WERE OBSERVED (MOST LIKELY DUE TO THE PRESENCE OF WATER OR OTHER NUCLEOPHILIC SPECIES).



**Scheme 2.** NITRATION OF DIMETHYLANILINE WITH THE PHOTOFRAGMENTATION PRODUCTS OF RDX AND PETN.

1 A DISTINCT ABSORBANCE BAND CENTERED AT 400 NM WAS FOUND TO ACCOMPANY THE FORMATION  
2 PRODUCTS UNDER BOTH AEROBIC AND ANAEROBIC CONDITIONS, WHICH ALSO MATCHED THE  
3 TRANSFER BAND DISPLAYED BY COMMERCIAL DMNA. HOWEVER, DMNA HAS A VERY LOW FLUORESCENCE  
4 YIELD<sup>17</sup> AND, THEREFORE, A SIGNIFICANT TURN-ON FLUORESCENCE SIGNAL IS NOT GENERATED  
5 WITH THE PHOTOFRAGMENTATION PRODUCTS OF RDX AND PETN.

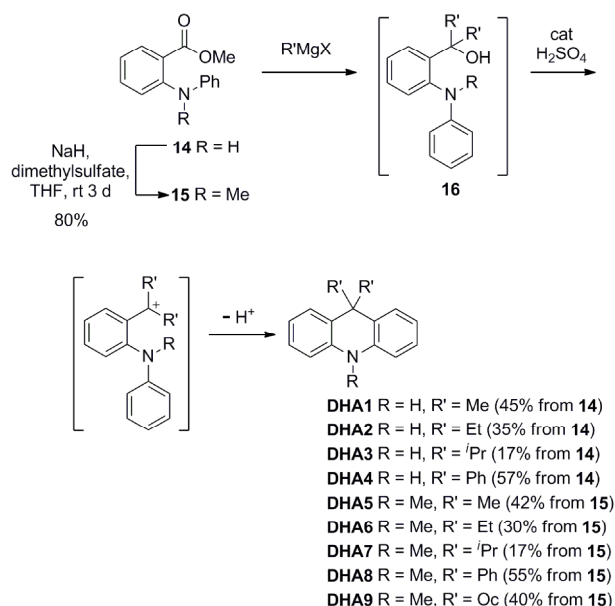
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7 TO PROBE THE SCOPE OF THE PHOTONITRATION REACTION, WE INVESTIGATED WHETHER 9,9-DIOCTYLFLUORENE  
8 AND 1,2-DIMETHOXYBENZENE COULD BE NITRATED BY RDX AND PETN. EXTENDED PHOTOLYSIS  
9 OF 9,9-DIOCTYLFLUORENE AND EITHER RDX OR PETN IN 1:1 ACETONITRILE:THF AT EITHER 254,  
10 NM FAILED TO GENERATE ANY OBSERVABLE PRODUCTS AND 9,9-DIOCTYLFLUORENE WAS RECOVERED  
11 PHOTOLYSIS OF ANISOLE WITH RDX OR PETN YIELDED ONLY TRACE AMOUNTS OF 4-NITROANISOLE  
12 AFTER 4 HOURS. PHOTOLYSIS OF 1,2-DIMETHOXYBENZENE WITH EITHER RDX OR PETN YIELDED  
13 NITROBENZENE IN ONLY CA. 8% YIELD AFTER 2 HOURS; MOREOVER THIS REACTION DID NOT  
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15 NUMEROUS POLAR PHOTOPRODUCTS WERE OBSERVED. THEREFORE, WE CONCLUDED THAT 9,9-DIOCTYLFLUORENE  
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17 CANDIDATES FOR A POTENTIAL INDICATOR.

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19 TO CREATE FLUOROGENIC INDICATORS BASED ON THE FACILE NITRATION REACTION BETWEEN  
20 THE PHOTOFRAGMENTATION PRODUCTS OF RDX AND PETN, 9,9-DISUBSTITUTED 9,10-DIHYDRO-9,10-ANTHRAQUINONE  
21 (FIGURE 2) WERE TARGETED AS CHEMOSENSORS. WE HYPOTHEZIZED THAT, UPON NITRATION, THE  
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23 DHAS WOULD GENERATE DONOR-ACCEPTOR CHROMOPHORES POSSESSING HIGH FLUORESCENCE.  
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27 **Synthesis.** AS SHOWN IN SCHEMES 3-5, A SERIES OF 9,9-DISUBSTITUTED DHAS WERE SYNTHESIZED  
28 FROM EITHER 9-PHENYLANTHRANILIC ACID METHYL ESTER (ROUTES A AND C) OR A DIPHENYLACETONE  
29 (ROUTE B). DHAS WERE ACCESSED BY AN ACID-CATALYZED CYCLIZATION OF A TERTIARY ALCOHOL  
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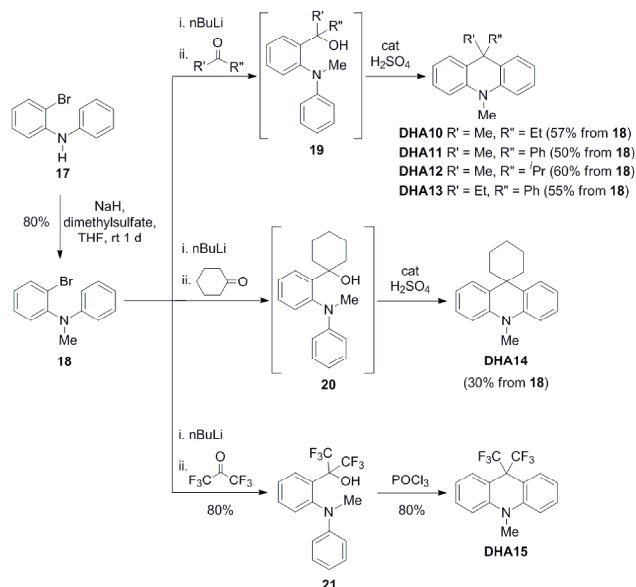
FROM 18 TO AN APPROPRIATE KETONE. THIS STRATEGY WAS ADOPTED TO SYNTHESIZE UNSYMMETRIC 9,10-DIHYDROACRIDINES (DHA10-13) THAT HAVE TWO DIFFERENT SUBSTITUENTS AT THE 9-POSITION, AND ALSO CONTAINING DHA (DHA15).

### Route A



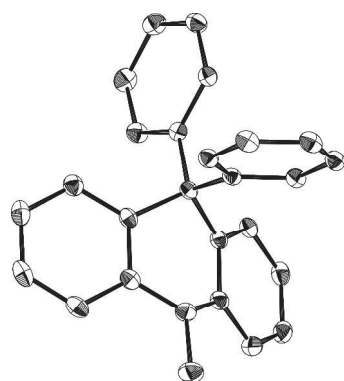
**Scheme 3.** ROUTE A FOR THE SYNTHESIS OF 9,9-DISUBSTITUTED 9,10-DIHYDROACRIDINES.

### Route B



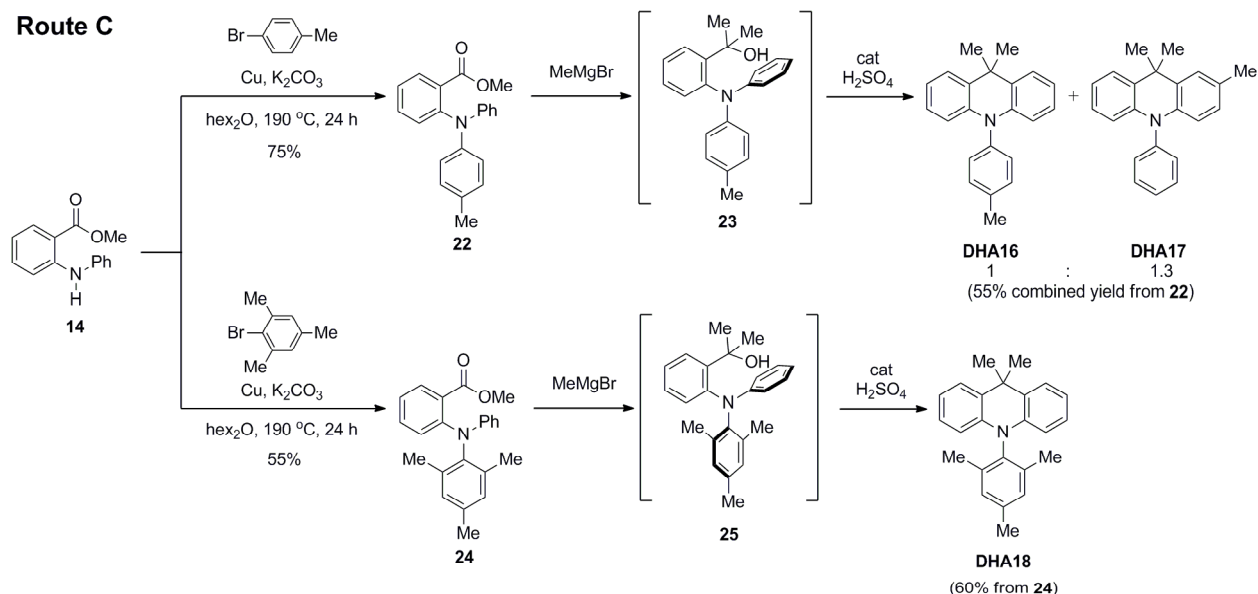
**Scheme 4.** ROUTE B FOR THE SYNTHESIS OF 9,9-DISUBSTITUTED DHAS.

IN ALL CASES EXCEPT ONE, ADDING A CATALYTIC AMOUNT OF CONCENTRATED SULFURIC ACID FACILITATES REACTION/CYCLIZATION OF THE RESPECTIVE TERTIARY ALCOHOL INTERMEDIATES DHAS. AS SHOWN IN SCHEME 3, WE POSIT THAT THIS TRANSFORMATION PROCEEDS VIA CARBOCATION. THE X-RAY CRYSTAL STRUCTURE OF **DHA8** OBTAINED IS SHOWN IN FIGURE 3. THE CYCLIZATION OF **DHA2** WAS UNIQUELY CHALLENGING, AS NEITHER THE USE OF STRONG ACIDS, LEWIS ACIDS, NOR TMS-CHLORIDE YIELDED **DHA5**.<sup>21</sup> HOWEVER, IT WAS FOUND THAT REFLUXING **DHA2** IN ACETONE PRODUCED **DHA15** IN HIGH YIELD.



**Figure 3.** X-RAY CRYSTAL STRUCTURE OF **DHA8**.

LASTLY, ROUTE C WAS FOLLOWED TO SYNTHESIZE **DHA18** (SCHEME 5). COPPER-CATALYZED CYCLIZATION OF **14** WITH 4-BROMOTOLENE INITIALLY YIELDED **22**, WHICH WAS THEN REACTED WITH 2.5 EQUIVALENTS OF METHYLMAGNESIUM BROMIDE AND CATALYTIC CONCENTRATED SULFURIC ACID. UNFORTUNATELY, CYCLIZATION OF INTERMEDIATE **22** YIELDED A NEARLY-STATISTICAL MIXTURE OF **DHA16** AND **DHA17** (1:1.3 **DHA16:DHA17**), WHICH COULD NOT BE ACCEPTABLY SEPARATED BY EITHER COLUMN CHROMATOGRAPHY OR RECRYSTALLIZATION. THEREFORE, **24** WAS SYNTHESIZED BY COPPER-CATALYZED CYCLIZATION OF **14** WITH 2-BROMOMESITYLENE AND SUBSEQUENTLY REACTED WITH METHYLMAGNESIUM BROMIDE TO ACCESS **DHA18**.



**Scheme 5.** ROUTE C FOR THE SYNTHESIS OF DHAS.

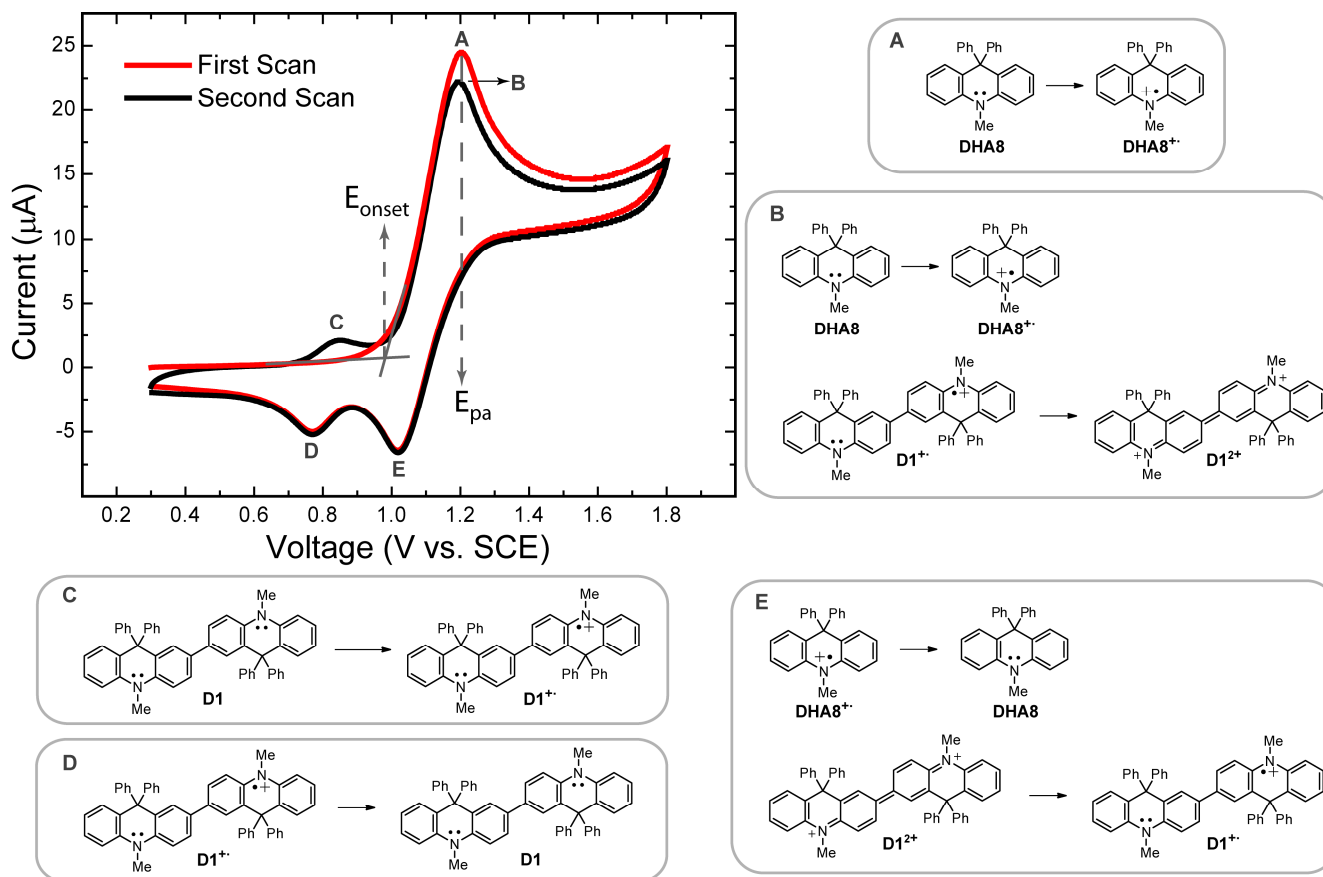
**Photophysics.** THE OPTICAL PROPERTIES OF DHAS 1-18 ARE SUMMARIZED IN TABLE 1. THE DHAS REPORTED HEREIN DISPLAYED SIMILAR UV-VIS ABSORPTION SPECTRA, WITH ABSORPTION MAXIMA ADDITIONALLY, DHAS 1-18 GENERALLY DISPLAYED A SINGLE EMISSION BAND CENTERED AT CA. 350 nm. DHAS 1-18 FOUND TO HAVE SIMILAR FLUORESCENCE QUANTUM YIELDS AND EXCITED-STATE LIFETIMES.

Table 1. OPTICAL PROPERTIES OF DHAS IN ACETONITRILE.

CMPD	$\lambda_{\text{MAX}}^{\text{ACN}}$ (LOG) $\epsilon$	$\lambda_{\text{EM}}^{\text{ACN}}$	$\Phi^{\text{A}}$	$\tau^{\text{B}}$ /NS
DHA1	284 (4.1)	352	0.18	2.7
DHA2	288 (4.1)	390	0.04	2.2
DHA3	288 (4.1)	376	0.09	2.7
DHA4	285 (4.0), 320 (3.8)	355	0.13	1.6
DHA5	285 (4.1)	355	0.14	2.8
DHA6	246 (4.1), 290 (4.0)	382	0.12	2.3
DHA7	257 (4.1), 298 (3.9)	345	0.10	2.7
DHA8	294 (3.9)	359	0.14	1.7
DHA9 <sup>B</sup>	247 (4.1), 290 (3.9)	345	0.15	2.8
DHA10	246 (4.3), 290 (4.1)	352	0.12	2.5
DHA11	289 (4.3)	355	0.14	1.7
DHA12	247 (4.0), 292 (3.9)	382	0.06	1.7
DHA13	245 (4.8), 296 (4.4)	355	0.09	2.2
DHA14	247 (4.0), 297 (3.8)	345	0.15	2.4
DHA15	280 (4.3), 311 (4.0)	354	0.18	2.5
DHA16 + DHA17	290 (4.2)	371	0.05	2.7
DHA18	290 (4.2)	371	0.03	2.5

<sup>A</sup> MEASURED AGAINST QUININE SULFATE IN 0.1N H<sub>2</sub>SO<sub>4</sub> IN THF  
<sup>B</sup> MEASURED AGAINST QUININE SULFATE IN 0.1N H<sub>2</sub>SO<sub>4</sub> IN THF





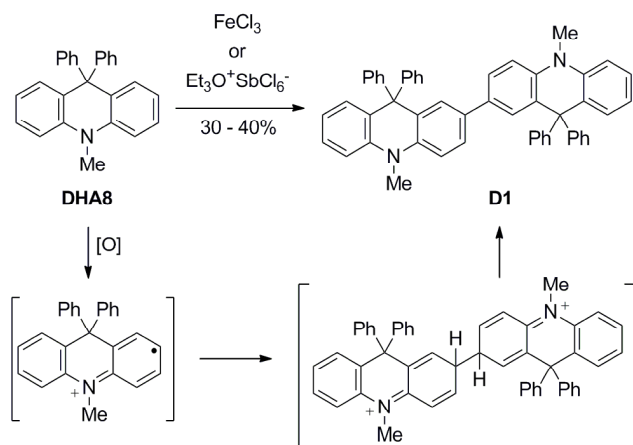
**Figure 4.** CYCLIC VOLTAMMOGRAMS OF DHA8 ON A GP-BT BUTTON ELECTRODE, 0.1 M TBAF<sub>4</sub>BF<sub>4</sub>, 100 MV/S.

THE REDOX REACTIONS GIVING RISE TO EACH ANODIC (A, B AND C) AND CATHODIC (D AND E) PEAK ARE SHOWN IN THE INSET. THE FIRST ANODIC PEAK POTENTIAL AND ONSET POTENTIAL FOR THE FIRST SCAN ARE LABELED.

**Electrochemistry.** CYCLIC VOLTAMMOGRAMS (CVS) OF SELECT DHAS WERE RECORDED IN 0.1 M TBAF<sub>4</sub>BF<sub>4</sub> AS SUPPORTING ELECTROLYTE AND WERE FOUND TO REVEAL BEHAVIOR SUGGESTIVE OF IRREVERSIBLE CHEMICAL TRANSFORMATIONS. IN THE CV OF DHA8 (FIGURE 4 AS A REPRESENTATIVE EXAMPLE). THE FIRST ANODIC SWEEP RESULTED IN A SINGLE ANODIC PEAK AT 1.20 V VS SCE, WHICH CAN BE ASCRIBED TO THE FORMATION OF THE DHA8<sup>+</sup>. HOWEVER, IN THE SECOND ANODIC SWEEP, TWO ANODIC PEAKS WERE OBSERVED. THE FIRST ANODIC PEAK WAS ASCRIBED TO THE OXIDATION OF DHA8<sup>+</sup> TO DHA8<sup>2+</sup>, WHILE THE SECOND ANODIC PEAK WAS ASCRIBED TO THE OXIDATION OF D1<sup>+</sup> TO D1<sup>2+</sup>. THE CORRESPONDING CATHODIC SWEEP REVEALED TWO CATHODIC PEAKS, ARISING FROM THE REDUCTION OF D1<sup>2+</sup> TO D1<sup>+</sup> AND DHA8<sup>2+</sup> TO DHA8<sup>+</sup>. FURTHERMORE, A SUBSEQUENT ANODIC SWEEP DISPLAYED TWO OXIDATION PEAKS, BEHAVIOR HAS BEEN PREVIOUSLY OBSERVED FOR TRIPHENYLAMINE, ATTRIBUTED TO THE RAPID DIMERIZATION OF TPA RADICAL CATIONS FOLLOWING OXIDATION; THE ELECTROACTIVE TPA D

TO THE GROWTH OF AN ADDITIONAL ANODIC AND CATHODIC PEAK AFTER AN INITIAL ANO  
 ASSIGNMENTS MADE FOR THE CV <sup>23</sup> OF THE REDOX REACTIONS RESPONSIBLE FOR THE INDIVIDUAL  
 CATHODIC PEAKS OBSERVED IN THE CV OF **DHA8** WERE IDENTIFIED AND ARE SHOWN IN FIGURE

THE DIMERIZATION OF RADICAL CATION OF ELECTROCHEMICAL **DHA8** WAS CONFIRMED BY  
 INDEPENDENTLY SYNTHESIZING **DHA8** WITH  $\text{FeCl}_3$  OR  $[\text{Et}_3\text{O}^+\text{SbCl}_6^-]$  <sup>23</sup> AFFORDING 30-  
 40% YIELD (SCHEME 6). THIS OXIDATION REACTION WAS FOUND TO SELECTIVELY YIELD THE D  
 TLC AND CRUDE NMR ANALYSES); MOREOVER, WE WERE ABLE TO RECOVER THE REMAINING, UN  
 UPON REACTION WORKUP. THE USE OF HYDROGEN PEROXIDE WAS ALSO  
 INVESTIGATED; HOWEVER, SUBSTANTIALLY FORMED IN LESS THAN 5% YIELD WITH THESE REA  
**DHA8** WAS RECOVERED IN CA. 90% YIELD AFTER REACTION WORKUP. ATTEMPTS TO AFF  
 POLYMERIZATION OF **DHA8** WERE NOT SUCCESSFUL AND WAS ISOLATED. THIS OBSERVATION CAN  
 EXPLAINED BY THE FACT THAT FORMED, CAN BE OXIDIZED TO A STABLE, CLOTTED, SHELL DICAT  
 FIGURE 3) THAT CANNOT PARTICIPATE IN SUBSEQUENT RADICAL COUPLING REACTIONS TO FOR  
 A FAINT-YELLOW COMPOUND THAT DISPLAYS AN ABSORPTION BAND CENTERED AT 457 NM A  
 CENTERED AT 478 nm (20). THE CV OF **D1** (SEE SUPPORTING INFORMATION) WAS FOUND TO MAT  
 SECOND SCAN OF THE CV OF **DHA8** (SEE FIGURE 4), THUS CONFIRMING THE AFOREMENTIONED ASSIGNM  
 ANODIC AND CATHODIC PEAKS OBSERVED IN THE CV OF **DHA8**.



**Scheme 6.** OXIDATIVE DIMERIZATION OF **DHA8** TO FORM **D1**.

THE ELECTROCHEMICAL BEHAVIOR OF DHA15 WAS SIMILAR TO THAT OF THE REST OF THE REPORTED DHAS. SIMILAR TO THE ELECTROCHEMICAL BEHAVIOR OF DMA—I.E., THE RESPECTIVE RADICAL CATIONIC ONSET POTENTIAL FOR THE FIRST ANODIC SWEEP. THE VALUES FOR THE FIRST ANODIC ONSET POTENTIAL FOR THE FIRST SCAN OF THE CVS OF SELECT DHAS, DMA AND TPA ARE SUMMARIZED IN TABLE 2. IN GENERAL, SIMILAR VALUES OF  $E_{\text{ONSET}}$  WERE OBSERVED FOR MOST DHAS; HOWEVER, ELECTRON-DEFICIENT DHA15 WAS AN OUTLIER AND DISPLAYED SIGNIFICANTLY HIGHER  $E_{\text{ONSET}}$  VALUES.

**Table 2.** ELECTROCHEMICAL PROPERTIES OF SELECT DHAS.

CMPD	$E_{\text{A}}$ /V VS SCE	$E_{\text{ONSET}}$ /V VS SCE
<b>DHA1</b>	1.19	0.77
<b>DHA2</b>	1.05	0.77
<b>DHA4</b>	1.07	0.87
<b>DHA5</b>	1.27	0.86
<b>DHA6</b>	1.30	0.86
<b>DHA7</b>	1.51	0.92
<b>DHA8</b>	1.20	0.95
<b>DHA9</b>	1.35	0.85
<b>DHA11</b>	1.08	0.87
<b>DHA15</b>	1.65	1.18
<b>DHA16 + DHA17</b>	1.04	0.83
<b>DHA18</b>	1.08	0.83
<b>DMA<sup>A</sup></b>	1.36	0.77
<b>TPA<sup>B</sup></b>	1.48	0.95

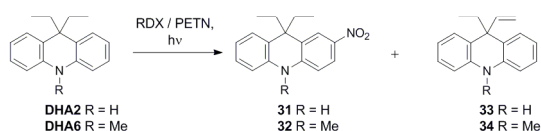
<sup>A</sup> *N,N*-DIMETHYLANILINE. <sup>B</sup> *p*-TRIPHENYLAMINE.

**Reaction with RDX/PETN Photofragmentation Products.** THE PHOTOREACTIONS ~~DHA18~~ AND EITHER RDX OR PETN WERE INITIALLY INVESTIGATED IN ACETONITRILE SOLUTIONS. IN SOLUTIONS CONTAINING ~~DHA18~~ AND EITHER RDX OR PETN (WHICH WERE INITIALLY COLORLESS) AND UNDER AEROBIC CONDITIONS LEAD TO THE EVOLUTION OF A BRIGHT YELLOW/ORANGE COLOR SECONDS TO 5 MINUTES. IRRADIATING ~~DHA18~~ IN THE ABSENCE OF EITHER RDX OR PETN DID NOT RESULT IN THE SAME BRIGHT YELLOW/ORANGE COLOR, ALTHOUGH FAINT YELLOWING OF ~~DHA18~~ WAS NOTICED AFTER GREATLY EXTENDED EXPOSURE (>60 MINUTES) TO UV LIGHT UNDER AEROBIC CONDITIONS.

THE PHOTOLYSES (313 NM) OF SELECT DHAS WITH A STOICHIOMETRIC AMOUNT OF EITHER RDX OR PETN WERE CONDUCTED ~~ON A~~<sup>Preparatory</sup> SCALE IN ORDER TO ISOLATE AND CHARACTERIZE THE REACTION PRODUCTS. IN THESE STUDIES, LONG IRRADIATION TIMES (GENERALLY 60 MINUTES) WERE EMPLOYED TO ACHIEVE REACTANT CONVERSION. TLC AND GC-MS ANALYSES OF CRUDE REACTION MIXTURES INDICATED THAT A HIGHLY-COLORED PRODUCT WAS FORMED IN ALL CASES. THE YELLOW-ORANGE PRODUCTS ~~DHA1, DHA4, AND DHA18~~ WITH EITHER RDX OR PETN WERE ISOLATED BY FLASH COLUMN CHROMATOGRAPHY AND IDENTIFIED TO BE THE MONO-NITRATED ~~STRUCTURES~~ (STRUCTURES 26, 28, AND 30, RESPECTIVELY) SHOWN IN SCHEME 7 BY <sup>1</sup>H NMR, FT-IR AND HIGH RESOLUTION MASS SPECTRA (SEE SUPPORTING INFORMATION). COMPOUNDS 26 AND 30 WERE ISOLATED IN 70-80% YIELD AFTER COLUMN CHROMATOGRAPHY, ALONG WITH CA. 10% OF ~~DHA1, DHA4, OR DHA18~~. SIMILARLY, ~~DHA5 AND DHA8~~ WERE CONFIRMED TO ~~BE~~<sup>PROANOL</sup>, RESPECTIVELY, IN APPROXIMATELY 70% YIELD (GC YIELD) UPON PHOTOLYSIS WITH RDX OR PETN. ADDITIONALLY, ~~DHA1 AND DHA4~~ WERE INDEPENDENTLY NITRATED UNDER MILD CONDITIONS USING <sup>24</sup> AND THE PRODUCTS THUS OBTAINED WERE FOUND TO MATCH THOSE ISOLATED ~~FROM~~ THE PHOTOLYSIS OF ~~DHA1 AND DHA4~~ WITH RDX/PETN.

**DHA1** R = H, R' = Me  
**DHA2** R = Me, R' = Me  
**DHA4** R = H, R' = Ph  
**DHA8** R = Me, R' = Ph  
**DHA18** R = 2-nesityl, R' = Me

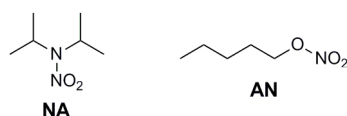
**26** R = H, R' = Me  
**28** R = Me, R' = Me  
**28** R = H, R' = Ph  
**29** R = Me, R' = Ph  
**30** R = 2-nesityl, R' = Me



**Scheme 7.** PHOTOREACTIONS OF VARIOUS 9,10-DIHYDROACRIDINES WITH RDX AND PETN. THE P  
OF RDX/PETN BY **AcrH** HAS BEEN PREVIOUSLY REPORTED.

THE PHOTOREACTION OF 33 WITH EITHER RDX OR PETN YIELDED THE NITRATED PRODUCT COMPOUND 33D WAS ALSO ISOLATED FROM THE REACTION MIXTURE (SCHEMES 1 AND 2). THE YIELD OF 33D WAS SOMEWHAT DEPENDENT ON THE CONCENTRATION OF 33, WITH HIGHER AMOUNTS OF 33 OBSERVED IN DILUTE SOLUTIONS. THE YIELD OF 33D WAS ALSO HIGHER RELATIVELY WHEN THE PHOTOLYSIS OF 33D AND RDX/PETN WAS CONDUCTED IN SLIGHTLY WET ACETONITRILE. COMPOUNDS 33D AND 33E WERE GENERALLY ISOLATED IN 80% COMBINED YIELD AFTER FLASH COLUMN CHROMATOGRAPHY OF THE REACTION MIXTURES, EITHER RDX OR PETN. FURTHERMORE, 33D WAS CONFIRMED TO BE 33D (BY GC-MS ANALYSIS) UPON PHOTOLYSIS IN THE PRESENCE OF RDX/PETN. WE HYPOTHESIZE THAT 33D IS FORMED AS A RESULT OF EITHER A HYDRIDE ABSTRACTION REACTION OF 33 BY RDX AND THE PHOTODEGRADATION PRODUCT OF RDX AND PETN. HOWEVER, WE ARE CURRENTLY UNSURE AS TO THE ORIGINS OF THE CONCENTRATION OF THE YIELD OF 33.

GC-MS ANALYSES OF THE PHOTOREACTIONS BETWEEN THE **DHA3**, **DHA6**, **DHA9**, **DHA10-17**) AND EITHER RDX OR PETN SIMILARLY REVEALED THE FORMATION OF MONO-NITRATED DERIVATIVES OF THE RESPECTIVE DHAS.



**Figure 5.** STRUCTURES OF A MODEL NITRAMINE, 1,1-DIMETHYL-2,2,2-TRINITROETHANE, AND A MODEL NITROESTER, AMYL NITRATE (

**Other Nitroesters and Nitramines.** THE PHOTOREACTIONS BETWEEN AND EITHER A MODEL NITRAMINE OR NITROESTER COMPOUNDS, 1,1-DIMETHYL-2,2,2-TRINITROETHANE AND AMYL NITRATE, RESPECTIVELY (FIGURE 5)—WERE ALSO INVESTIGATED. THE REACTION PRODUCTS OBSERVED UPON PHOTOLYSIS OF MIXTURES OF 1-18 AND EITHER ORAN WERE IDENTICAL (AS ESTABLISHED BY TLC AND GC ANALYSES) TO THE AFOREMENTIONED NITRATED PRODUCTS OBSERVED WITH RDX AND PETN. OBSERVED YIELDS (GC YIELDS) OF NITRATED DHAS WERE SIGNIFICANTLY LOWERED TO RDX/PETN. FOR EXAMPLE, WHEREAS WAS FORMED IN 75% YIELD UPON PHOTOLYSIS WITH EITHER PETN FOR 30 MINUTES, THE PHOTOLYSIS OF AN ORAN AFFORDED IN ONLY 30% YIELD UNDER IDENTICAL REACTION CONDITIONS. THEREFORE, IT CAN BE TENTATIVELY INFERRED THAT RDX IS MORE SUSCEPTIBLE TO PHOTOLYTIC CLEAVAGE THAN THEIR RESPECTIVE MODEL COMPOUNDS.

**Differences in DHA Reaction Mechanisms.** AS SHOWN IN SCHEME 7, IT IS INTERESTING TO NOTICED A DIFFERENCE IN PHOTOCHEMICAL REACTION MECHANISMS BETWEEN VARIOUS 9,10-DIHYDROACETONITRILES. REPORTEDLY, METHYL-9,10-DIHYDROACETONITRILE PARTICIPATES IN A HYDRIDE TRANSFER REACTION WITH RDX, PETN, NA ORAN. DIAALKYLATION OR DIARYLATION OF THE ACETONITRILE GROUP EFFECTIVELY NULLIFIES ITS ABILITY TO DONATE A HYDRIDE ION AND PROMOTES THE PHOTONITRATION REACTION DETAILED IN SCHEME 7.

**Light Sources.** IMPORTANTLY, PRECISE TIMING AND SOPHISTICATED, HIGH-INTENSITY LIGHT SOURCES WERE FOUND TO BE NECESSARY TO EFFECT THE REACTIONS AND THE DEGRADATION PRODUCTS OF RDX AND PETN.



1 RDX OR PETN. SIMPLY EXPOSING A MIXTURE OF RDX/PETN TO POLYCHROMATIC LIGHT FROM  
2 SOLAR SIMULATOR EFFECTED THE PHOTOLYTIC CLEAVAGE OF RDX/PETN AND SUBSEQUENT  
3 NITRATED DHAS. FOR EXAMPLE, COMPOUNDS 26 AND 28 COULD BOTH BE ISOLATED IN 75% YIELD (AFTER  
4 COLUMN CHROMATOGRAPHY) AFTER A MIXTURE OF RDX OR PETN AND RESPECTIVELY, IN  
5 ACETONITRILE WERE EXPOSED TO SIMULATED SUNLIGHT FOR 45 MINUTES. THE YIELDS OF COM  
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OBTAINED ARE SIMILAR TO THOSE REPORTED EARLIER FOR PHOTOLYSIS AT 313 NM.

**Other NO<sub>x</sub> Sources.** THE (PHOTO)REACTIONS OF RDX WITH SODIUM NITRITE, POTASSIUM NITRATE  
NO WERE ALSO INVESTIGATED TO JUDGE THE LIMITATIONS OF USING-OFF INDICATORS FOR  
RDX/PETN. EXPOSING A MIXTURE OF DHA1, DHA5, DHA4 OR DHA8 AND EXCESS SODIUM NITRITE IN  
2:1 ACETONITRILE:WATER TO SIMULATED SUNLIGHT FOR 2 HOURS DID NOT RESULT IN SIGNIFI  
DHAS (<1% GC YIELDS 26-29 WERE GENERALLY OBSERVED). HOWEVER, UPON ADDITION OF 100  
ACID TO THE SAME REACTION MIXTURE 26-29 WERE FORMED IN APPROXIMATELY 8% YIELD IN  
*absence* OF LIGHT. PROTONATING NITRITE SALTS GENERATES NITROUS ACID, WHICH IS KNOWN TO  
HNO<sub>3</sub> (AMONG OTHER SPECIES), WHICH MOST LIKELY NITRATED THE DHAS IN THIS CASE.

THE ADDITION OF A LARGE EXCESS OF MONOMERIC NO GAS TO DRY, OXYGEN-FREE  
AFOREMENTIONED DHAS FAILED TO GENERATE THE CHARACTERISTIC YELLOW ORANGE COLOR  
INTRODUCTION OF OXYGEN TO THESE SOLUTIONS, THE NITRATED DHAS WERE OBSERVED TO B  
ABSENCE OF LIGHT). SUBSEQUENT GC-MS ANALYSES 26-29 WERE FORMED IN CA. 20% YIELD.  
ONCE AGAIN, NO IS KNOWN TO FORM NITROGEN DIOXIDE UPON EXPOSURE TO OXYGEN, WHICH  
IN NITRATION OF THE DHAS.

MIXTURES DHA1, DHA5, DHA4 OR DHA8 AND A LARGE EXCESS OF POTASSIUM NITRATE  
ACETONITRILE:WATER DID NOT IMMEDIATELY RESULT IN NITRATION 26-29, EVEN STANDING FOR  
MULTIPLY-NITRATED DERIVATIVES OF THE AFOREMENTIONED DHAS, WERE FORMED IN LESS TH  
(GC YIELD). ADDING ACETIC ACID TO MIXTURES RESULTED IN THE FORMATION OF MULTIPL  
DHAS, WITH 2,7-DINITRO DHAS BEING THE MAJOR PRODUCTS. EXPOSING MIXTURES OF EITHER

**DHA4 OR DHA8** AND A LARGE EXCESS OF POTASSIUM NITRATE IN 2:1 ACETONITRILE:WATER TO FOR 60 MINUTES SIMILARLY YIELDED MULTIPLY-NITRATED DERIVATIVES OF THESE DHAS IN COMBINED YIELD. STOICHIOMETRIC OR SUB-STOICHIOMETRIC AMOUNTS OF POTASSIUM IRRADIATION TIMES FAILED TO GENERATE OBSERVABLE QUANTITIES OF NITRATED DHAS.

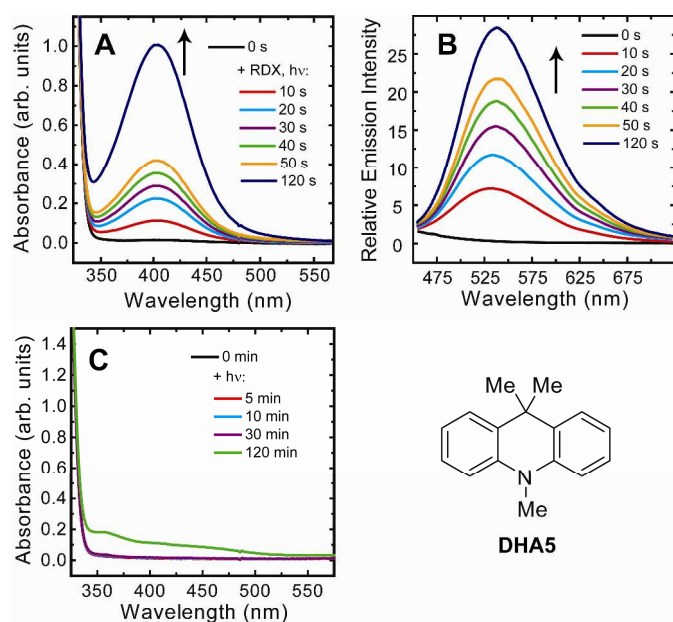
**Optical Properties of Nitrated DHAs.** THE PHOTOPHYSICAL PROPERTIES OF SELECT NITRATED DHAS WERE EITHER ISOLATED FROM THE PHOTOLYSIS REACTIONS BETWEEN DHAS AND RDX/PETN OR BY NITRATING AN APPROPRIATE DHA, ARE LISTED IN TABLE 3. IN GENERAL, THE NITRATED DHAS SHOW ABSORBANCE BANDS AS DMNA, WITH THE LOWEST ENERGY BANDS CENTERED AT CA. 400 NM. EMISSION BANDS CENTERED AT CA. 540 NM WERE OBSERVED FOR ALL ISOLATED MONO-NITRATED DHAS. FLUORESCENCE QUANTUM YIELDS OF THE COMPOUNDS LISTED IN TABLE 3 WERE FOUND TO RANGE FROM 0.05 TO 0.45, WITH THE LOWEST QUANTUM YIELDS OBSERVED FOR COMPOUNDS **26**, **28**, **30** AND **31** WERE FOUND TO DISPLAY SIGNIFICANT EMISSION IN THE SOLID STATE (IN CELLULOSE ACETATE FILM OF THE APPROPRIATE COMPOUND).

**Table 3.** OPTICAL PROPERTIES OF SELECT MONO-NITRATED DHAS.

CMPD	$\lambda_{MAX}^A$ (LOG) $\epsilon$	$\lambda_{EM}^A$	$\Phi$
<b>DMNA</b>	395 (3.9)	530	<0.01 (MECN) <sup>B</sup> 0.09 (CHCl <sub>3</sub> ) <sup>B</sup> 0.17 (FILM) <sup>D</sup>
<b>26</b>	408 (4.1)	535	0.09 (MECN) <sup>B</sup> 0.27 (CHCl <sub>3</sub> ) <sup>B</sup> 0.35 (FILM) <sup>D</sup>
<b>28</b>	410 (4.1)	540	0.10 (MECN) <sup>B</sup> 0.30 (CHCl <sub>3</sub> ) <sup>B</sup> 0.42 (FILM) <sup>D</sup>
<b>30</b>	413 (4.2)	548	0.14 (MECN) <sup>B</sup> 0.37 (CHCl <sub>3</sub> ) <sup>B</sup> 0.45 (FILM) <sup>D</sup>
<b>31</b>	409 (4.1)	539	0.05 (MECN) <sup>B</sup> 0.22 (CHCl <sub>3</sub> ) <sup>B</sup> 0.33 (FILM) <sup>D</sup>

<sup>A</sup> IN MECN <sup>B</sup> MEASURED AGAINST PERYLENE IN 10 WT% IN CELLULOSE ACETATE  
 AGAINST 10 WT% PERYLENE IN PMMA (

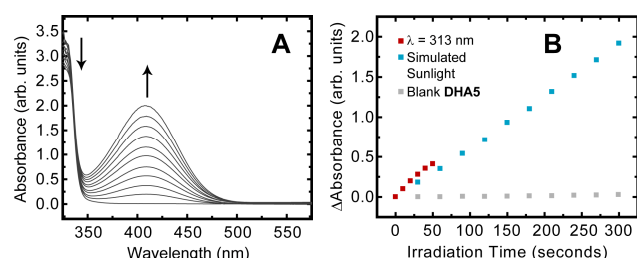
**Optical Characterization of Indicator Response.** THE ABSORPTION AND EMISSION PROFILES FOR  
 REACTION BETWEEN DHA5 AND RDX UNDER AEROBIC CONDITIONS ARE SHOWN IN FIGURE 6. AN ABSO  
 CENTERED AT CA. 408 NM WAS OBSERVED TO INCREASE (408 NM) WITH RDX, WHICH  
 CORRESPONDS TO THE FORMATION OF EMISSION BAND AT APPROXIMATELY 540 NM CONCOMITANTLY  
 WHICH CAN BE ASSIGNED TO EMISSION FROM THE EMISSION PROFILE RECORD FOR  
 26. A CA. 27-FOLD INCREASE IN THE EMISSION INTENSITY AT 540 NM WAS GENERATED AFTER  
 IRRADIATION. EXACTLY SIMILAR ABSORPTION AND EMISSION PROFILES WERE OBTAINED I  
 BETWEEN DHA5 AND PETN. MOREOVER, THE PRESENCE OR ABSENCE OF OXYGEN DID NOT NOTICE  
 OBSERVED OPTICAL RESPONSE.



**Figure 6.** ABSORPTION (A) AND EMISSION (B, 540 NM) PROFILES OF THE PHOTOREACTION OF  
 RDX IN ACETONITRILE UPON IRRADIATION DHA5,  $1.3 \times 10^{-4}$  M. [RDX] =  $5.4 \times 10^{-5}$  M. IDENTICAL  
 PROFILES ARE OBSERVED FOR THE PHOTOREACTION OF THE PRESENCE OR ABSENCE OF OXYO  
 SIMILARLY DOES NOT AFFECT THE OBSERVED ABSORPTION AND EMISSION PROFILES. THE ABS  
 EXTENDED IRRADIATION OF A BLANK, AERATED SOLUTION OF DHA5 IS ALSO SHOWN (C).

PHOTOLYSIS OF **DHA5** UNDER AEROBIC CONDITIONS IN THE ABSENCE OF RDX/PETN FAILED TO  
 DISTINCT ABSORBANCE BAND AT 408 NM. SURPRISINGLY, HOWEVER, IT WAS FOUND TO BE RELATIVELY  
 PHOTOSTABLE: 30 MINUTES OF CONTINUOUS UV IRRADIATION DID NOT RESULT IN A NOTICEABLE  
 ABSORPTION SPECTRUM (FIGURE 6C), AND ITS EMISSION PEAK AT 355 NM (SEE TABLE 1) WAS FOUND  
 TO BE BLEACHED BY ONLY 10%. FURTHER UV IRRADIATION EVENTUALLY LED TO SOLUTIONS YELLOW  
 AND POORLY-DEFINED ABSORBANCE PEAKS AT 356 NM AND CA 440 NM APPEARED IN THE ABSORPTION  
 AFTER 2 HOURS OF CONTINUOUS UV IRRADIATION UNDER AIR (FIGURE 6C). THESE NEW ABSORBANCE  
 LIKELY CORRESPOND TO THE FORMATION OF RADICAL CATION SPECIES, AND OTHER DERIVATIVES  
 OF **DHA5**. NOTABLY, THOUGH, A SIGNIFICANT PORTION OF THIS PHOTOLYZED **DHA5** SOLUTION REMAINED  
 AFTER 2 HOURS, AND, THEREFORE, THE SUBSEQUENT ADDITION OF RDX OR PETN NONETHELESS  
 A 408 ABSORBANCE PEAK AND 540 NM EMISSION PEAK (5-FOLD EMISSION TURN-ON) AFTER A 20 MINUTE  
 EXPOSURE TO 313 NM LIGHT.

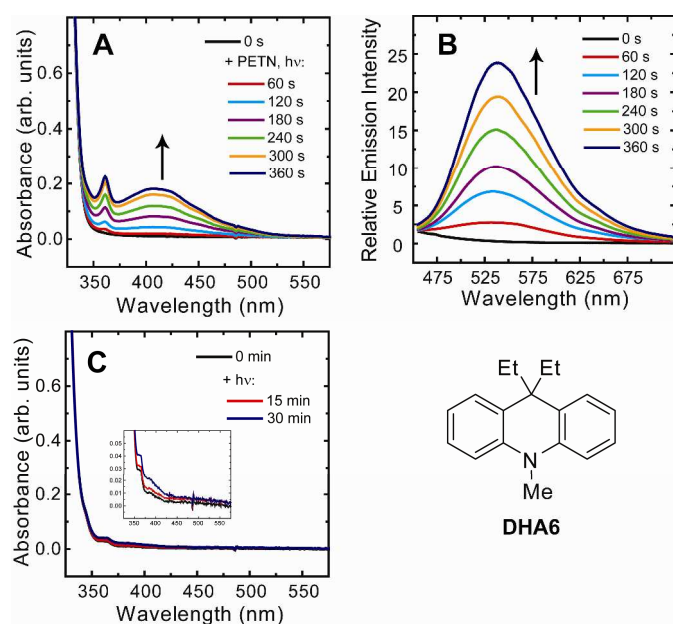
AS SEEN IN FIGURE 7, EXPOSING A MIXTURE OF **DHA5** AND RDX TO BROAD-BAND LIGHT FROM A SOLAR  
 LEAD TO THE EVOLUTION OF THE SAME 408 NM PEAK OBSERVED WITH IRRADIATION AT 313 NM. THE  
 FORMATION OF THE 408 NM PEAK UPON EXPOSURE TO SIMULATED SUNLIGHT ALSO MATCHED THE  
 EXPOSURE TO MONOCHROMATIC 313 NM LIGHT FROM A XENON ARC LAMP (FIGURE 7B). THE  
 SUNLIGHT WAS PREFERENTIALLY USED AS THE LIGHT SOURCE IN SUBSEQUENT STUDIES TO PERFORM  
 FUNCTION AS TECHNOLOGY-UNINTENSIVE, FLUOROGENIC INDICATORS FOR RDX/PETN UNDER A



**Figure 7.** (A) ABSORPTION PROFILE OF THE PHOTOPRODUCT OF **DHA5** AND RDX IN ACETONITRILE UPON EXPOSURE  
 TO BROAD-BAND LIGHT FROM A SOLAR SIMULATOR.  $[DHA5] = 1.0 \times 10^{-5}$  M.  $[RDX] = 5.4 \times 10^{-5}$  M. (B) THE RATE OF

FORMATION OF THE 408 NM ABSORBANCE PEAK IN THE PRESENCE OF RDX UPON EXPOSURE TO SUNLIGHT OR MONOCHROMATIC 313 NM LIGHT.

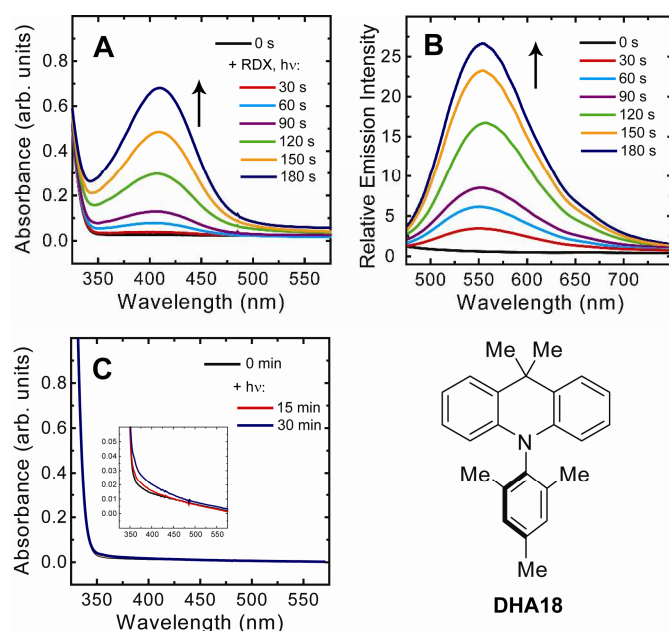
THE ABSORPTION AND EMISSION PROFILES FOR THE REACTION BETWEEN PETN AND RDX UPON EXPOSURE TO SIMULATED SUNLIGHT ARE SHOWN IN FIGURE 8. DHA6 BEHAVES SIMILARLY TO DHA5 IN TERMS OF ITS OPTICAL RESPONSE. SPECIFICALLY, AN ABSORBANCE PEAK AT 409 NM EVOLVED IN THE PRESENCE OF RDX ACCOMPANIED WITH EVOLUTION OF AN EMISSION BAND AT 540 NM. THE PRESENCE OR ABSENCE OF RDX DOES NOT AFFECT THE OBSERVED OPTICAL RESPONSE. DHA6 WAS ALSO FOUND TO BE RELATIVELY PHOTOINERT WITH NO CHANGE IN ITS ABSORPTION SPECTRUM AND A 5% BLEACHING OF ITS EMISSION BAND OBSERVED AFTER 30 MINUTES OF CONTINUOUS EXPOSURE TO SUNLIGHT. THE ONLY SIGNIFICANT DIFFERENCE BETWEEN DHA5 AND DHA6 WAS THE RATE OF FORMATION OF THE 409 NM /540 NM ABSORPTION/EMISSION BAND. DHA6 WAS FOUND TO YIELD A TURN-ON SIGNAL APPROXIMATELY THREE TIMES FASTER THAN DHA5. THIS COMPARATIVELY SLOW RESPONSE FOR DHA6 IS BECAUSE A MIXTURE OF DHA6 AND RDX UPON REACTING WITH RDX/PETN (SEE SCHEME 7). COMPOUND 32 IS RESPONSIBLE FOR THE 409 NM/540 NM ABSORPTION/EMISSION BANDS, WHEREAS 34 IS NOT GREEN-FLUORESCENT AND IS RESPONSIBLE FOR THE 356 NM ABSORPTION BAND. FIGURE 8A.



**Figure 8.** ABSORPTION (A) AND EMISSION (B, 540 NM) PROFILES OF THE PHOTOREACTION OF PETN IN ACETONITRILE UPON EXPOSURE TO SIMULATED SUNLIGHT.  $[[\text{PETN}]] = 5.4 \times 10^{-5}$

M. THE ABSORPTION PROFILE FOR THE EXTENDED IRRADIATION OF A **DHA18** IN ACETONITRILE SOLUTION IS SHOWN (C).

THE OPTICAL RESPONSE OF **DHA18** TO EITHER RDX OR PETN (FIGURE 9) WAS SIMILAR TO THAT OF **DHA5**. AN ABSORBANCE BAND AT 413 NM AND AN EMISSION PEAK AT 550 NM EVOLVED UPON EXPOSURE TO SUNLIGHT IN THE PRESENCE OF EITHER RDX OR PETN. ALSO RELATIVELY PHOTOSTABLE, WITH A MINOR CHANGE IN ITS ABSORPTION SPECTRUM AND A 5% BLEACH OF ITS EMISSION BAND AT 371 NM OBSERVED AFTER CONTINUOUS EXPOSURE TO SIMULATED SUNLIGHT FOR 30 MINUTES. THE RATE OF PHOTOREDUCTION OF **DHA18** WITH RDX/PETN WAS SLOWER THAN THAT OF **DHA5** BUT FASTER THAN THAT OF **DHA6**.

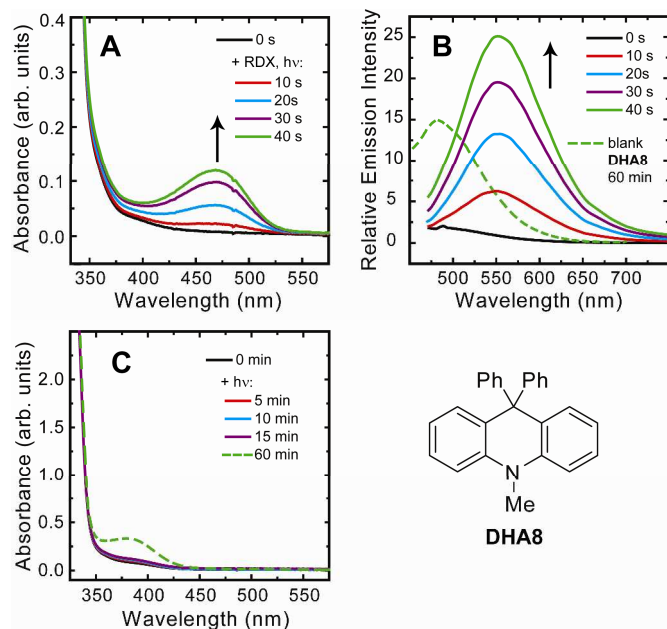


**Figure 9.** ABSORPTION (A) AND EMISSION (B) PROFILES OF THE PHOTOREDUCTION OF **DHA18** IN ACETONITRILE IN THE PRESENCE OF RDX (5.4  $\times 10^{-5}$  M) UPON EXPOSURE TO SIMULATED SUNLIGHT. THE ABSORPTION PROFILE FOR THE EXTENDED IRRADIATION OF A **DHA18** IN ACETONITRILE SOLUTION IS SHOWN (C).

9,9-DIPHENYL-SUBSTITUTED **DHA18** DIFFERED SLIGHTLY FROM THE OTHER DHAS EXPLORED IN THIS STUDY. AN ABSORBANCE BAND CENTERED AT 470 NM, AS OPPOSED TO CA. 410 NM, EVOLVED DURING ITS EXPOSURE TO SUNLIGHT IN THE PRESENCE OF EITHER RDX OR PETN (FIGURE 10). BASED ON ACCOMPANYING GC-MS ANALYSES, THIS ABSORBA



BE ASSIGNED TO THE FORMATION OF AN EMISSION BAND AT 550 NM WAS ALSO OBSERVED TO CONCOMITANTLY. AN APPROXIMATELY 25-FOLD INCREASE IN THE EMISSION INTENSITY AT 550 NM IN THE PRESENCE OF EITHER RDX OR PETN UPON EXPOSURE TO SIMULATED SUNLIGHT FOR 40 SECONDS. REACTION OF **DHA5** AND **DHA8** WITH RDX/PETN WERE APPROXIMATELY SIMILAR.



**Figure 10.** ABSORPTION (A) AND EMISSION (B) PROFILES OF THE PHOTOREACTION OF **DHA8** WITH RDX IN ACETONITRILE UPON EXPOSURE TO SIMULATED SUNLIGHT.  $[\text{RDX}] = 5.4 \times 10^{-5} \text{ M}$ . THE DASHED GREEN LINE DEPICTS THE EMISSION SPECTRUM OBTAINED FOR A BLANK SOLUTION OF **DHA8** AFTER 60 MIN OF IRRADIATION UNDER EITHER AEROBIC OR ANAEROBIC CONDITIONS. THE ABSORPTION SPECTRA OF **DHA8** AFTER 60 MIN OF IRRADIATION OF A BLANK, AERATED SOLUTION IS ALSO SHOWN (C); THE SAME PROFILE IS ALSO OBTAINED FOR ANAEROBIC, OXYGEN-FREE SOLUTIONS OF **DHA8**.

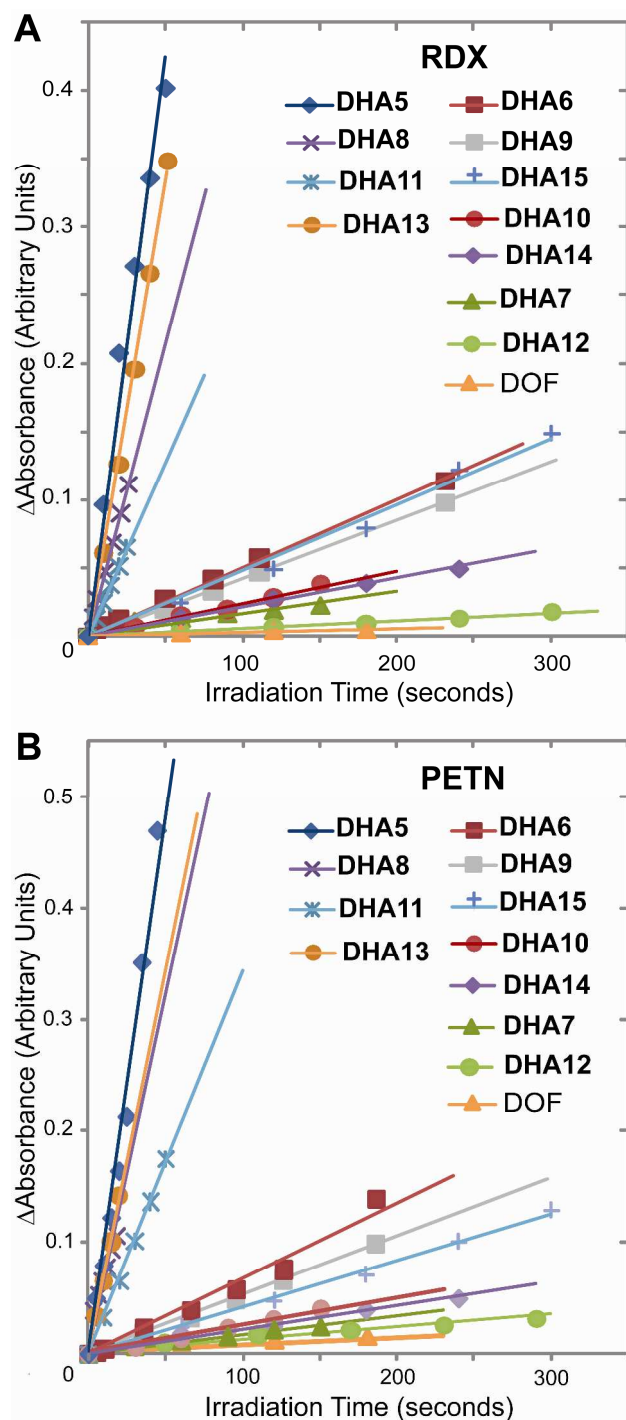
UNLIKE **DHA5**, **DHA6** AND **DHA18**, EXPOSING SOLUTIONS OF **DHA8** TO SUNLIGHT (OR MONOCHROMATIC LIGHT) IN EITHER THE PRESENCE OR ABSENCE OF OXYGEN LEAD TO THE FORMATION OF A DISTINCT EMISSION BAND AT 550 NM, WITH AN ACCOMPANYING ABSORPTION BAND CENTERED AT 380 NM. THE SAME PHOTOREACTION WAS OBSERVED FOR OTHER DHAS THAT CONTAINED AT LEAST ONE PHENYL SUBSTITUENT IN THE 9,9-POSITION (**DHA9**, **DHA11** AND **DHA13**). SINCE THESE ABSORPTION/EMISSION BANDS WERE OBSERVED TO EVOLVE

1 ABSENCE OF OXYGEN, THEY ARE MOST LIKELY NOT GENERATED BY SIMPLE ~~DHAS~~ OXIDATION.  
2  
3 MOREOVER, THE EVOLUTION OF THE ABSORBANCE BAND AT 380 NM CANNOT BE ASCRIBED TO  
4  
5 EVENT, AS THE PRODUCT OF SUCH ~~REACTIONS~~, HAS AN ABSORPTION MAXIMUM OF 457 NM. WE  
6  
7 CURRENTLY UNSURE AS TO THE ORIGIN OF THE PHOTOPRODUCT RESPONSIBLE FOR THE  
8  
9 ABSORPTION/EMISSION PEAK BUT SUSPECT THAT A PHOTOCYCLIZATION REACTION OCCURS IN THE  
10  
11 PHENYL SUBSTITUENT IN THE 9-POSITION. NEVERTHELESS, FOR THE PURPOSES OF THIS WORK, IT  
12  
13 10 THAT THE COMPETING PHOTOREACTION IN BLANK SOLUTIONS OF ~~DHAS~~ IS LOWER THAN THE PHOTONITRATION  
14  
15 **DHA8** IN THE PRESENCE OF RDX/PETN AND AN EMISSION PEAK AT 550 NM IS CLEANLY GENERATED  
16  
17  
18  
19 EXPLOSIVES IN UNDER 10 SECONDS.

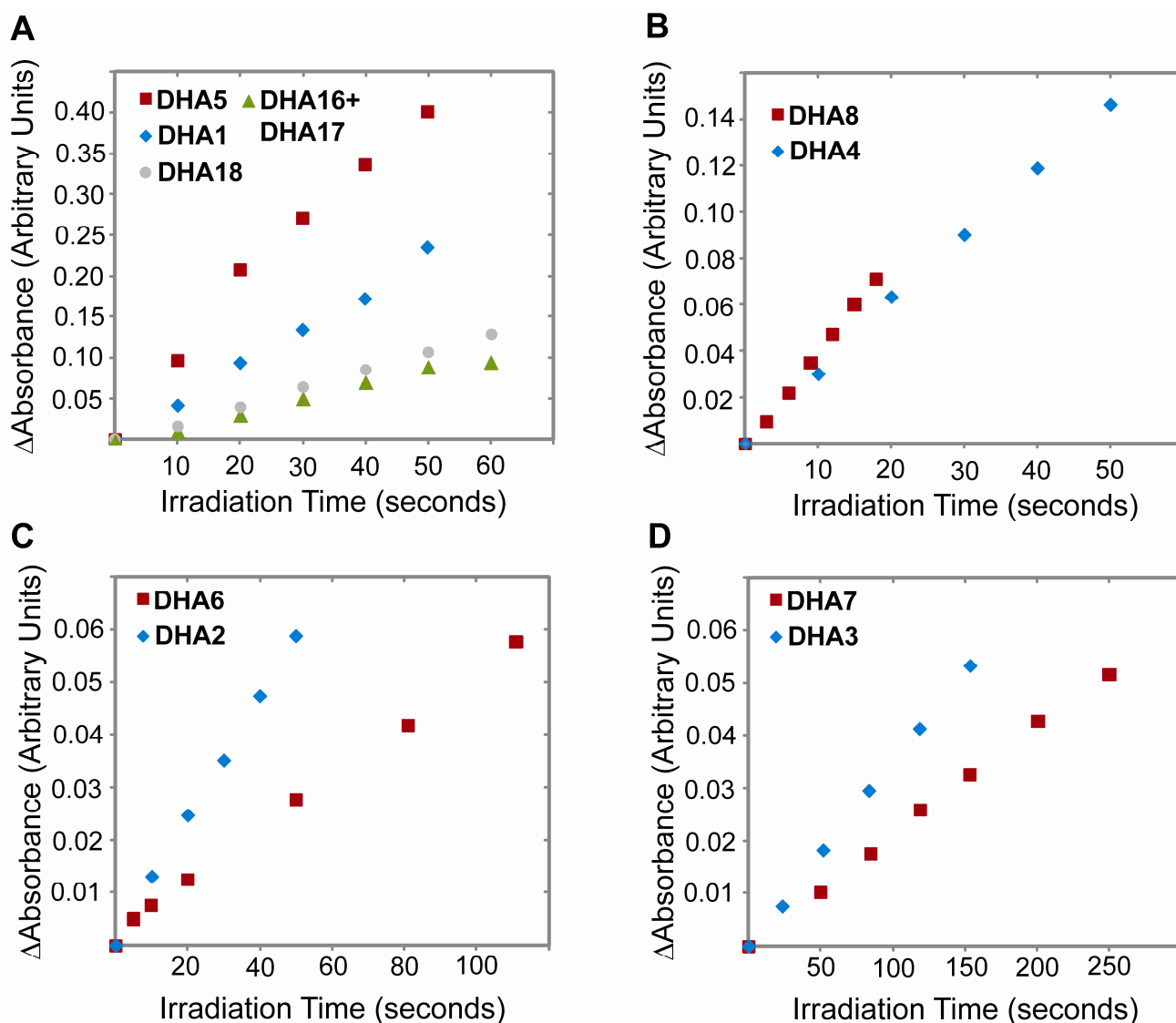
20  
21  
22  
23  
24 **Reaction Kinetics.** THE MOST SIGNIFICANT DIFFERENCE BETWEEN THE DHAS REPORTED IN THIS  
25  
26 THE RATE OF FORMATION OF THE NITRATED PHOTOPRODUCTS UPON REACTION WITH RDX OR PETN  
27  
28 EVOLUTION OF THE CHARACTERISTIC LOW-ENERGY CHARGE TRANSFER BAND (CENTERED AT 400 NM)  
29  
30 DHAS WITH IRRADIATION TIME, WE WERE ABLE TO IDENTIFY DIFFERENCES IN THEIR REACTIVITIES  
31  
32  
33 11 AND 12). AS CAN BE SEEN IN FIGURE 11, THE SUBSTITUENTS AT THE 9-POSITION OF DHAS SIGNIFICANTLY  
34  
35 THEIR REACTIVITIES. DHAS WITH AT LEAST ONE METHYL OR PHENYL SUBSTITUENT AT THE 9-POSITION  
36  
37 NITRATED IN THE PRESENCE OF RDX OR PETN. DHAS WITH ALKYL (OTHER THAN METHYL) SUBSTITUENTS  
38  
39 POSITION DISPLAYED RELATIVELY SLOWER RATES OF NITRATION, WITH ISOPROPYL SUBSTITUENTS  
40  
41 REACTION RATES. REPLACING THE 9-METHYL SUBSTITUENTS WITH TRIFLUOROMETHYL MOVED TO  
42  
43 REACTION RATE. NOMINALLY FASTER REACTION RATES WERE GENERALLY OBSERVED WITH  
44  
45 DHAS. 9,9-DIOCTYLFLUORENE WAS USED AS A NEGATIVE CONTROL FOR THESE STUDIES AND, IN  
46  
47  
48  
49 REPORTED IN THIS WORK YIELDED A SIGNIFICANT ABSORPTION SIGNAL AT 400 NM OVER BACKGROUND  
50  
51

52 THE NATURE OF THE SUBSTITUENT WAS ALSO FOUND TO AFFECT THE RATE OF PHOTONITRATION  
53  
54 RDX/PETN. AS SEEN IN FIGURE 12, FOR DHAS WITH ETHYL OR ISOPROPYL SUBSTITUENTS AT THE 9-POSITION  
55  
56 N-H ANALOGUES REACTED FASTER THAN THEIR N-ANALOGUES. FOR DHAS WITH PHENYL OR METHYL SUBSTITUENTS  
57  
58  
59  
60

9-POSITION, THIS TREND WAS REVERSED AND DOF DISPLAYED THE FASTEST REACTION RATES. IN THE PHOTOREACTIONS WITH PETN, **DHA5** AND **DHA15** DISPLAYED THE FASTEST REACTION RATES. **N**-ARYLATION WAS FOUND TO SIGNIFICANTLY RETARD THE RATE OF PHOTONITRATION.

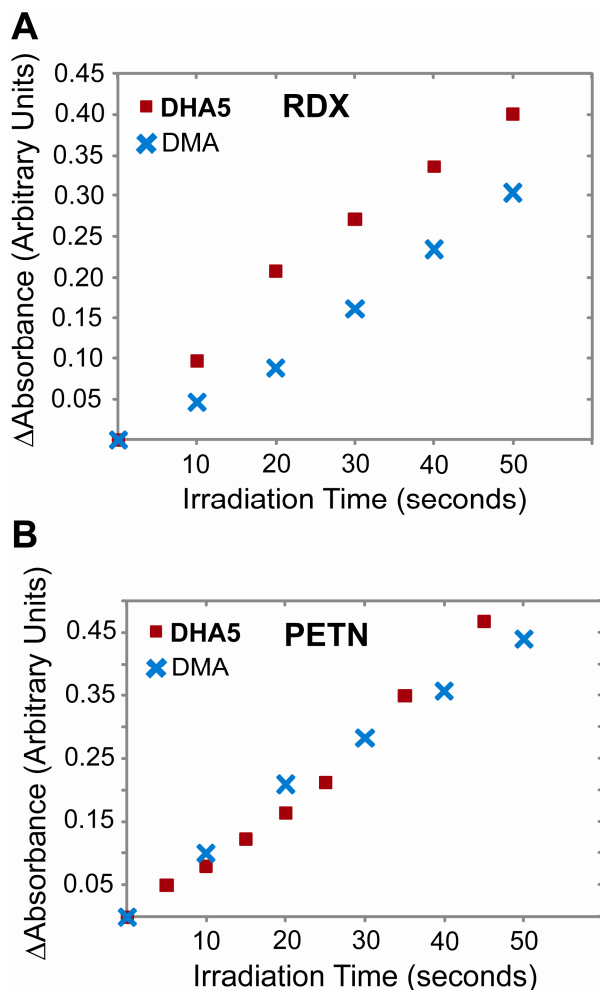


**Figure 11.** THE EFFECT OF THE SUBSTITUENTS AT THE 9-POSITION OF DHAS ON THEIR PHOTOREACTIONS WITH RDX AND PETN. SHOWN ARE THE RATES OF EVOLUTION OF THE ABSORBANCE PEAKS FOR **DHA5** AND **DHA15** IN THE PHOTOREACTIONS WITH RDX OR (B) PETN. DOF IS 9,9-DIOCTYLFLUORENE, WHICH WAS USED AS A NEGATIVE CONTROL.



**Figure 12.** THE EFFECT OF SUBSTITUENT OF DHAS ON THEIR PHOTOREACTIONS WITH RDX. SHOWN ARE THE RATES OF EVOLUTION OF THE ABSORBANCE PEAK AT 410 NM FOR THE PHOTOREACTIONS BETWEEN VARIOUS DHAS AND RDX.

LASTLY, THE RATE OF FORMATION OF NITRATED DHAS WAS COMPARED TO THE FORMATION OF DMA. AS SEEN IN FIGURE 13, THE REACTION OF DHA5, WHICH DISPLAYED THE FASTEST RATE OF NITRATION, IS COMPARABLE TO THAT OF DMA.

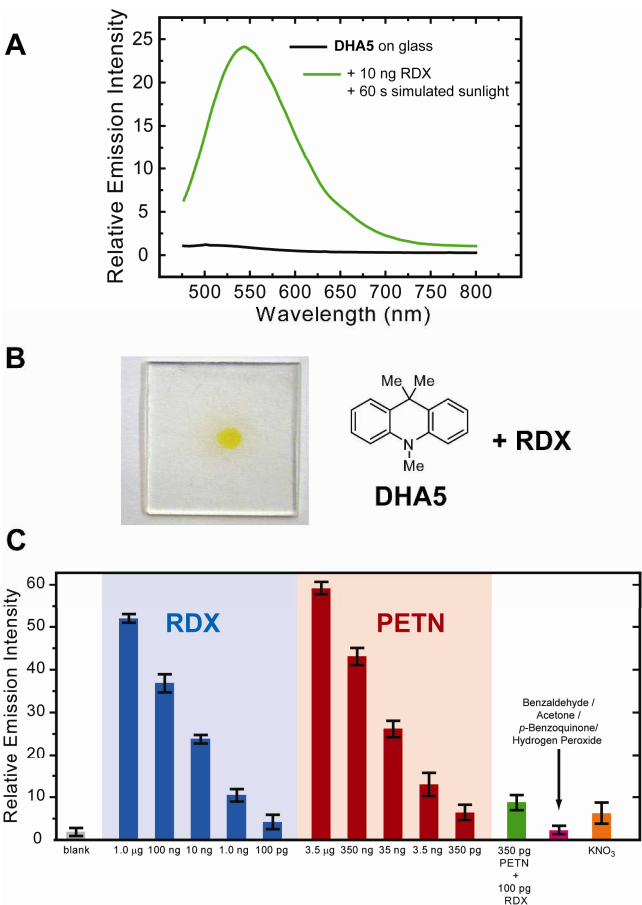


**Figure 13.** COMPARISON OF THE RATES OF **DHA5** AND **DMA** IN THE PRESENCE OF (A) RDX OR (B) PETN.

**Solid State RDX/PETN Detection.** BASED ON THE PREVIOUSLY-DETAILED RATES OF IRRADIATION OF **DHA5** AND **DMA** BY THE PHOTOFRAGMENTATION PRODUCTS OF RDX AND PETN, WE INITIALLY FOCUSED ON **DHA5** AND **DMA** AS POTENTIAL INDICATORS FOR RDX AND PETN, AS THEY DISPLAYED THE FASTEST REACTION. BETWEEN THESE FOUR, **DHA5** AND **DMA** WERE FAVORED BECAUSE THEIR NITRATED PRODUCTS DISPLAYED HIGH FLUORESCENCE QUANTUM YIELDS. EACH OF THESE INDICATORS DEMONSTRATED DETECTION OF RDX/PETN IN THE SOLID STATE; HOWEVER, SIMILAR RESULTS AND DETECTION LIMITS WERE OBTAINED WITH **DHA8**.

IN ORDER TO EVALUATE THE **DHA5** AS A FLUORESCENT INDICATOR FOR RDX AND PETN, THE SOLID-STATE RESPONSE OF **DHA5** TO RDX AND PETN WAS INVESTIGATED. FOR THIS STUDY, GLASS SLIDES COATED WITH **DHA5** WERE USED.

WERE PREPARED BY DIPCOATING INTO SOLUTIONS OF THE INDICATOR IN ACETONITRILE AND AIR DRYING. RDX AND PETN SOLUTIONS OF VARYING CONCENTRATION WERE SPOTTED ONTO THE SURFACE AND TREATED WITH A SOLAR SIMULATOR FOR NO LONGER THAN 120 SECONDS.



**Figure 14.** (A) EMISSION PROFILE (420-800 NM) OF A GLASS SLIDE COATED WITH DHA5 (BLACK LINE) AND THE SAME SLIDE AFTER SPOTTING WITH CA. 10 NG OF RDX AND IRRADIATING WITH A SOLAR SIMULATOR (GREEN LINE). (B) PICTURE OF A GLASS SLIDE SPOTTED WITH CA. 10 NG RDX AND EXPOSED TO SIMULATED SUNLIGHT FOR 120 S. (C) LIMITS OF SOLID-STATE DETECTION OF RDX AND PETN BY MONITORING THE CHANGE IN EMISSION INTENSITY AT 540 NM UPON EXPOSURE TO SIMULATED SUNLIGHT.

AS SHOWN IN FIGURE 14A, AN ACCEPTABLE TURN-ON EMISSION SIGNAL AT 540 NM WAS GENERATED BY RDX AFTER 60 SECONDS OF IRRADIATION WITH A SOLAR SIMULATOR. IN ADDITION TO A FLUORESCENT DISTINCT YELLOW COLOR, A YELLOW COLOR COULD ALSO BE OBSERVED BY EYE, AS SHOWN IN FIGURE 14B. THE LIMITS OF DETECTION OF DHA5 CHEMOSENSOR WERE ESTIMATED BY SPOTTING RDX OR PETN SOLUTIONS

CONCENTRATIONS ~~ON~~ COATED SLIDES AND ARE SHOWN IN FIGURE 12C. IN GENERAL, A GREAT  
SIGNAL AT 540 NM WAS GENERATED BY PETN OVER RDX, POSSIBLY BECAUSE PETN IS MORE  
PHOTODEGRADATION THAN RDX.

SELECT INTERFERENTS, SUCH AS KETONES AND ALDEHYDES, DID NOT PRODUCE A SIGNIFICANT  
NM. MOREOVER, CONSISTENT WITH OBSERVATIONS MADE DURING HYDROPEROXIDE DID NOT  
REACT READILY ~~AND~~ AND MOST LIKELY ONLY FORMED A SMALL QUANTITY OF ~~DH~~ RADICAL  
WHICH IS NON-EMISSIVE AND THEREFORE DID NOT PRODUCE ANY EMISSION AT 540 NM.

AQUEOUS POTASSIUM NITRATE SOLUTIONS OF VARYING CONCENTRATIONS ~~WERE~~ ALSO SP  
COATED GLASS SLIDES IN ORDER TO GAUGE THE ~~RESPONSE~~ OF THE NITRATE CONTAMINATION  
CONSISTENT WITH PREVIOUS OBSERVATIONS, SUB-MICROMOLAR SOLUTIONS OF POTASSIUM NI  
SIGNIFICANT EMISSION SIGNAL AT 540 NM AFTER ONE HOUR IN EITHER THE ABSENCE OF PRESE  
IRRADIATION. USING A 30 MM SOLUTION OF POTASSIUM NITRATE, AN APPROXIMATELY 8-F  
EMISSION INTENSITY AT 540 NM WAS OBSERVED AFTER A 10 MINUTE EXPOSURE TO SIMULATED  
GIVEN THE HIGH NITRATE CONCENTRATION AND RELATIVELY LONG IRRADIATION TIME NECES  
SIGNAL, INTERFERENCE FROM NITRATES DURING RDX/PETN DETECTION CAN, IN THEORY, BE SUP

WITHIN EXPERIMENTAL ERROR, APPROXIMATELY 100 PG OF RDX AND PETN ~~CAN~~ BE DETECTED  
INDICATOR UNDER AEROBIC CONDITIONS BY MONITORING THE EMISSION INTENSITY AT 540 NM  
NITRATE INTERFERENTS, THIS DETECTION LIMIT IS CONSERVATIVELY ESTIMATED AS CA. 1 NG  
ALTHOUGH NOT LOW ENOUGH FOR THE DETECTION OF EQUILIBRIUM VAPOR, ARE COMMON  
TRANSPORTATION SECURITY SYSTEMS THAT MAKE USE OF SWIPES TO COLLECT PARTICLES.

## Conclusions

WE HAVE FOUND THAT THE NITRAMINE-CONTAINING EXPLOSIVE RDX AND THE NITROESTER  
PETN ARE SUSCEPTIBLE TO PHOTOFRAGMENTATION UPON EXPOSURE TO SUNLIGHT, ~~PRODUCING~~  
SUCH AS NITROGEN DIOXIDE AND NITROETHYLANILINE AND 9,9-DISUBSTITUTED 9

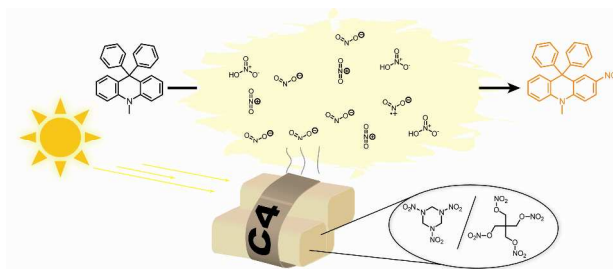


DIHYDROACRIDINES (DHAS) ARE CAPABLE OF BEING SELECTIVELY NITRATED BY THE REACT  
PHOTOFRAGMENTATION PRODUCTS OF RDX AND PETN. THIS NITRATION REACTION PROCEED  
ONLY ONE MAJOR, SINGLY-NITRATED PRODUCT. A ROUGHLY 25-FOLD INCREASE IN THE EMISSION  
OBSERVED UPON NITRATION OF DHAS DUE TO THE GENERATION OF FLUORESCENT DONOR-ACC  
MONITORING THE EMISSION INTENSITY AT CA. 550 NM, THE PRESENCE OF APPROXIMATELY 100 P  
CAN BE DETECTED WITHIN ONE MINUTE BY THESE INDICATORS IN THE SOLID STATE UPON EX  
PHOTONITRATION REACTION PRESENTED HEREIN IS A UNIQUE AND SELECTIVE DETECTION MEC  
NITRAMINE EXPLOSIVES THAT IS DISTINCT FROM A PREVIOUSLY-REPORTED PHOTOREDUCT  
EXPLOSIVES. THE RAPID NITRATION OF 9,9-DIPHENYL OR -DIMETHYL SUBSTITUTED DHA CH  
PRESENCE OF RDX OR PETN AND THE RESULTING STRONG, TURN-ON EMISSION SIGNAL QUALI  
CHEAP, IMPERMANENT INDICATORS FOR THE SELECTIVE, STANDOFF IDENTIFICATION OF NI  
EXPLOSIVES.

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SCIENCE FOUNDATION (ECCS – 0731100).

**Supporting Information Available.** EXPERIMENTAL PROCEDURES, SPECTRAL CHARACTERIZATIO  
CRYSTALLOGRAPHIC INFORMATION FILE.

## TOC graphic.



9,9-DISUBSTITUTED 9,10-DIHYDRIACRIDINES (DHAS) ARE NITRATED BY THE PHOTOFRAGMENTATION OF HIGH EXPLOSIVES RDX AND PETN. THE DONOR-ACCEPTOR CHROMOPHORES THUS GENERATED HAVE HIGH ABSORPTION COEFFICIENTS AND MODERATE FLUORESCENCE QUANTUM YIELDS AND, THEREFORE, GENERATE A FLUORESCENCE SIGNAL. 1.2 NG OF RDX AND 320 PG OF PETN CAN BE DETECTED BY DHAS IN THE SOLID STATE UNDER SUNLIGHT. THE NITRATION REACTION IS PRESENTED AS A UNIQUE AND SELECTIVE DETECTION METHOD FOR NITRAMINE EXPLOSIVES AND DHAS ARE PRESENTED AS CHEAP AND IMPERMANENT DETECTORS FOR THE SELECTIVE, STANDOFF IDENTIFICATION OF RDX AND PETN.

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